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Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
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EPA-600/3-77-008
January 1977

SECOND ANNUAL CATALYST RESEARCH PROGRAM REPORT

Summary

by

Criteria and Special Studies Office
Health Effects Research Laboratory
Research Triangle Park, N.C. 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, N.C. 27711

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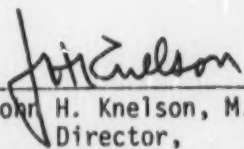
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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory develops and revises air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is preparing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

New technologies for controlling emissions of pollutants to the atmosphere are always a welcome advance in the pursuit of a cleaner environment through research. A thorough study of these new technologies is in order, however, to assure that the net effect on public health is beneficial. The Catalyst Research Program, in its investigation of the automotive oxidation catalyst, provides a sound base upon which the EPA can make a responsible assessment of the effect on public health of this advanced emission control technology.



John H. Knelson, M.D.
Director,

Health Effects Research Laboratory

PREFACE

The Catalyst Research Program, initiated in FY 1975, is a broad multidisciplinary research effort to provide a sound technical basis for evaluating the public health issues related both to the benefits associated with the reduction of regulated emissions and to the potential health hazards associated with any unregulated emissions generated by control systems. This report covers work performed during the second year of the Catalyst Research Program plus related work performed outside the CRP.

ABSTRACT

This report constitutes the second Annual Report of the ORD Catalyst Research Program required by the Administrator as noted in his testimony before the Senate Public Works Committee on November 6, 1973. It includes all research aspects of the broad multidisciplinary program including: emissions characterization, measurement method development, monitoring, fuel analysis, toxicology, biology, epidemiology, human studies, and unregulated emissions control options. Principal focus is upon catalyst-generated sulfuric acid and noble metal particulate emissions.

Highlights in this report are:

- Sulfuric acid emissions from production catalyst-equipped vehicles are lower than those predicted in the first Annual Report.
- Pre-catalyst baseline data on platinum levels in the environment and in representative populations are reported.
- Increases in sulfate concentrations near a freeway have been observed.
- Data on ultrafine sulfuric acid emitted from production catalyst-equipped vehicles are presented.

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I. INTRODUCTION

Section 202 of the Clean Air Act of 1970, as amended, required substantial reduction in certain specified emission products from automobiles. The automotive industry, to achieve these reductions, chose the oxidation catalytic converter as a primary method of emission control for model year 1975. Subsequent to this decision, EPA intensified its research program to determine what, if any, new pollutants might be emitted into the atmosphere as a result of the application of this technology. Also studied were the effects of fuel composition and fuel additives on these, as well as regulated, emissions. Results from the EPA research program indicated that though emissions of hydrocarbons, carbon monoxide, and certain organics would be dramatically lowered, sulfuric acid aerosol emissions would increase, and slight emissions of platinum, palladium, and alumina might also be expected.

Because existing ambient concentrations of sulfates in many areas of the country have been shown to be at levels sufficient to cause concern, and because very little information existed regarding health effects of platinum or palladium as air pollutants, EPA initiated a broad research program to examine the public health impact of catalyst-emitted sulfates, platinum, and palladium.

In testimony to the Public Works Committee of the U.S. Senate, Administrator Train specified EPA's planned program of catalyst-related research:

1. Accelerate work on development of a reliable test procedure for automotive sulfate emission measurement.
2. Consider all feasible alternatives for automotive sulfate emission control.
3. Improve the Agency's ability to estimate the public health impact of sulfate and other automotive emissions.
4. Improve understanding of the atmospheric chemistry involved in these emissions and initiate an appropriate air monitoring program.

From these broad objectives defined in Administrator Train's testimony of November 1973, an extensive interdisciplinary research program was developed utilizing the resources of EPA's technical staff in the Office of Research and Development and the Office of Air and Waste Management as well as extramural programs with the scientific community outside the government. The first eighteen months of effort in the program have been completed. The initial results of the program were summarized in the first annual report published as EPA report #EPA-600/3-75-010a-j (10 volumes) dated September 1975. This report is the second in a series planned for annual issuance through at least 1977.

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The second report differs slightly from the first report in the organization of material with the contents arranged according to the laboratory organization under whose management the work was performed. This change was made in order to facilitate both reporting requirements and identification of responsible program management for follow-up requests for further information from report users.

Four supplements to the summary portion of this annual report cover work performed as part of the Catalyst Research Program by the following groups: Health Effects Research Laboratory, Research Triangle Park, N.C. (Supplement I); Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C. (Supplement II); Environmental Sciences Research Laboratory, Research Triangle Park, N.C. (Supplement III); and the Health Effects Research Laboratory, Cincinnati, Ohio (Supplement IV). A fifth supplement covers related work performed by the Office of Mobile Source Air Pollution Control, Washington, D.C. (Supplement V). Overviews of each organization's programs are included in both this summary report and within each supplement. In addition, Figure 1 provides a brief overview of the research responsibilities of the five organizations participating in the Catalyst Research Program.

Readers familiar with the first Catalyst Research Program Annual Report may wish to follow up on progress of projects included previously as individual tasks within specific discipline areas. For this purpose, a crosswalk listing of projects as treated in the 1975 annual report with references to their status as of the current reporting period is provided as Appendix A to this summary.

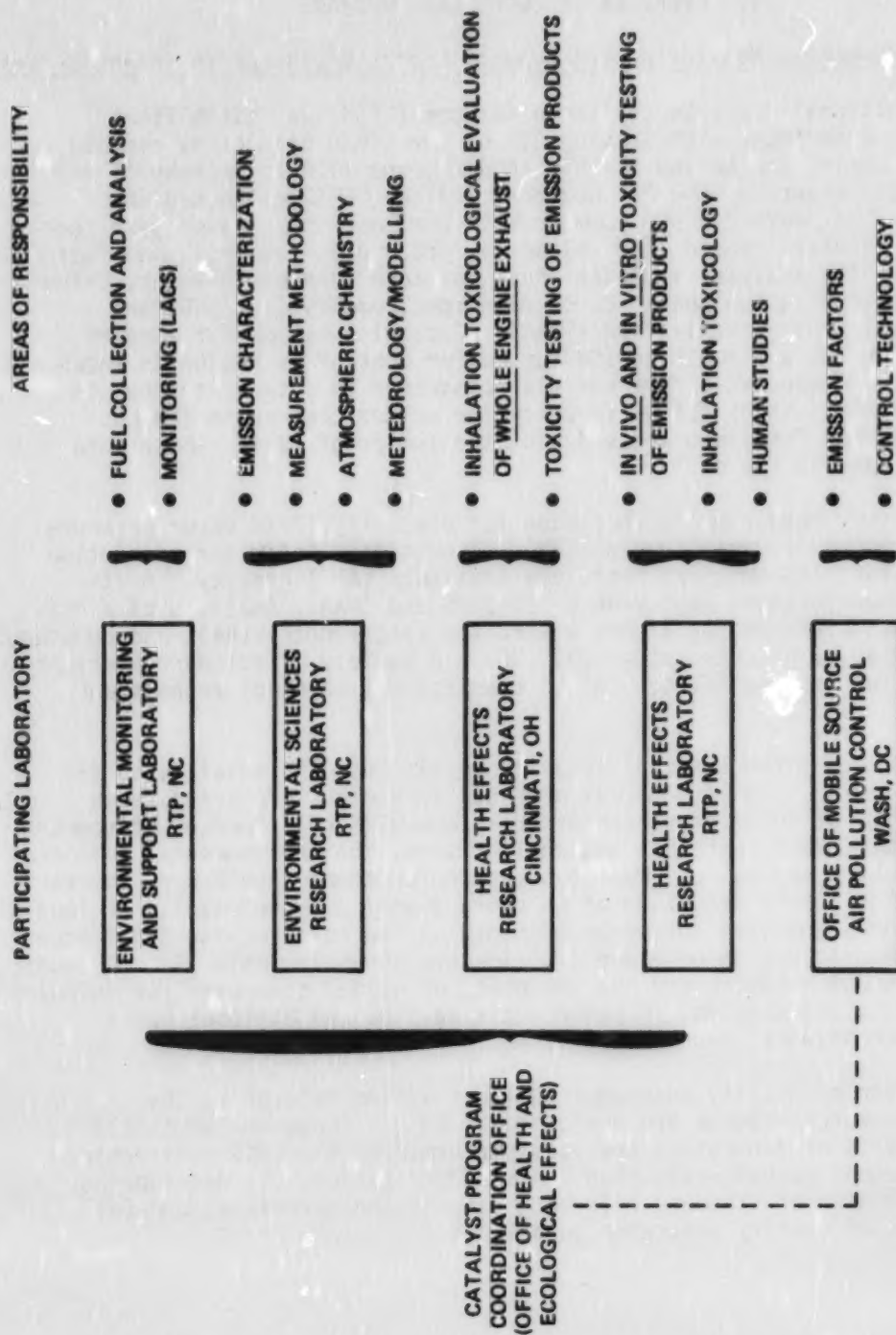


Figure 1. Organization of the Catalyst Research Program

II. OVERVIEW OF COMPONENT PROGRAMS

A. Environmental Monitoring and Support Laboratory/Research Triangle Park

The National Fuels Surveillance Network (NFSN) was established in 1972 in accordance with Section 211 of the Clean Air Act as amended in 1970. During the period of this report (June 1974 to December 1975) with the assistance of the EPA Regional Offices, EMSL collected and analyzed approximately 3,000 commercially purchased samples of gasoline (premium, regular, leaded, and unleaded), motor oil, fuel oil, and fuel additives. The analyses included those for more than one element, using both isotopic dilution spark source mass spectrometry (ID-SSMS) and instrumental neutron activation (INAA). Typical analyses for samples collected during a 6-month period for sulfur content by region is shown in Table I. A special effort was also conducted in support to the Los Angeles Catalyst Study (LACS) to determine sulfur content in the Los Angeles and San Francisco areas during the summer of 1974. These data are summarized in Table II.

Accessory measurements were made for viscosity, Reid vapor pressure (RVP), carbon-hydrogen-nitrogen (CHN), fluorescence indicator adsorption (FIA), sulfur, and American Petroleum Institute (API) gravity. Multi-element determinations were made by ID-SSMS and INAA. Analysis of single elements was performed by atomic absorption spectrometry (AA), and compounds were analyzed by gas chromatography (GC). A variety of standard American Standards and Testing Methods (ASTM) chemical and physical methods was also used.

There were three areas of activity within the NFSN relating to the catalyst program. Assistance was provided to various EPA groups such as the Office of Enforcement and General Counsel/Mobile Source Enforcement Division (OEGC/MSED), the EPA regional offices, the Environmental Sciences Research Laboratory (ESRL), Mobile Source Enforcement, Ann Arbor, and the joint New York State-EPA study of unleaded gasoline. The results of lead and phosphorus analyses during an 18-month period to determine compliance with the regulations on unleaded gasoline are shown in Table III. A study was carried out to determine the integrity of welded seam cans for shipping unleaded gasoline samples. A paper entitled "The EPA National Fuels Surveillance Network" was also published.

A number of quality assurance (QA) activities related to the Catalyst Research Program are performed by EMSL. These include: (1) routine audits of laboratory analyses performed by the LACS contractor, (2) measurement method evaluation and standardization, (3) development and distribution of standard reference samples and materials, and (4) preparation of quality assurance guidelines.

TABLE I

Sulfur Content of Unleaded Gasoline
Summary by Region - June-November 1974

<u>Region</u>	<u>Total Samples</u>	<u>Weight Percent Sulfur</u>		
		<u>Minimum</u>	<u>Maximum</u>	<u>Average</u>
I	24	0.004	0.089	0.029
II	14	0.009	0.042	0.023
V	22	0.005	0.094	0.031
VI	23	0.005	0.073	0.035
VII	22	0.001	0.075	0.037
VIII	23	0.004	0.052	0.023
IX	8	0.006	0.076	0.018

TABLE II

A Comparison of Sulfur Content in Gasoline
by Grade in Los Angeles and San Francisco
Summer 1974

	<u>San Francisco</u>	<u>Los Angeles</u>
Premium		
No. Samples	19	19
Wt. %S	0.009	0.026
Regular		
No. Samples	15	12
Wt. %S	0.035	0.051
Unleaded		
No. Samples	18	16
Wt %S	0.027	0.034
Low Lead		
No. Samples	2	2
Wt %S	0.009	0.042

TABLE III

Lead and Phosphorus Content in Unleaded Gasoline
June 1974-December 1975

Region	No. Samples	Violations	
		Pb	P
I	19	0	0
II	16	7	0
III	23	0	0
IV	56	6	0
V	81	0	0
VI	48	1	0
VII	67	8	1
VIII	35	2	1
IX	22	1	0
X	19	0	3

The routine audit program consists of sending the LACS contractor blind quality control audit samples on a routine schedule to be analyzed with the contractor's normal analyses. Audit samples for sulfate ($\text{SO}_4^{=}$), nitrate (NO_3), and lead (Pb) analyses are sent weekly and those for sulfur dioxide (SO_2) are sent bi-weekly. Tables IV and V summarize a portion of the $\text{SO}_4^{=}$ and Pb audit sample analyses performed by the LACS contractor. Brief summaries of the contractor's accuracy and standard deviation are prepared and distributed every five weeks to EPA personnel concerned with LACS. A summary report for general distribution is prepared every three months.

A measurement methods evaluation and standardization program for ambient aerosol $\text{SO}_4^{=}$ has been initiated. The work is organized into three phases, namely: (1) a thorough literature survey of methods for ambient $\text{SO}_4^{=}$ measurement and a recommendation of two methods for complete evaluation; (2) an in-depth laboratory familiarization of the two methods; and (3) a statistically designed experimental program (sometimes called ruggedness testing) to detect the effect of a number of important variables on each method. At present the literature survey has nearly been completed and a summary document is being prepared. The methythymol blue (MTB) and the barium chloranilate methods have been selected for further investigation.

EMSL has cooperated with ASTM Committee D2 in collaborative tests of the analysis procedures for phosphorus (P) and lead (PB) in unleaded gasoline. The collaboratively tested methods are ASTM D-3231 and ASTM D-3237, respectively.

In order to support QA programs, a variety of National Bureau of Standards (NBS) Standard Reference Materials (SRM) and EPA Standard Reference Samples (SRS) have been prepared. These reference samples and materials are used for calibration checks by measurement method operators and quality control audits by operators' supervisors. In cooperation with NBS, SRM's and SRS's have been developed for Pb in unleaded gasoline. These SRM's and SRS's have been distributed to the Regional Offices as part of an EMSL QA technical support effort to the Mobile Source Enforcement Division for the enforcement of the Pb and P fuel regulation. A bulk sample of sulfur (S) in unleaded gasoline was also developed. This will be packaged and distributed upon request. SRS's for Pb, $\text{SO}_4^{=}$, and NO_2 on glass fiber filters were also developed as well as a freeze-dried liquid sample of sodium sulfite (NaSO_3) for auditing the chemical analysis portion of the manual SO_2 measurement method.

EMSL has prepared a variety of quality assurance guidelines both on the establishment of QA programs and on specific measurement methods used with the Catalyst Research Program. A quality assurance plan was prepared for the Mobile Source Enforcement Division for sample collection and analysis of Pb and P during the enforcement of the fuels regulation. Measurement method guidelines were completed and published in the Environmental Monitoring Series for: (1) a laboratory method for determination of Pb in gasoline; (2) a field method for determination of Pb in gasoline; and (3) a laboratory method for determination of P in gasoline.

TABLE IV

Summary of LACS Contractor (Rockwell) Analyses
of Blind Sulfate QC Samples

<u>Sample ($\mu\text{g SO}_4$)</u>	<u>RISC Mean ($\mu\text{g SO}_4$)</u>	<u>% Difference</u>	<u>Mean Range</u>	<u>% Mean Range</u>
181	264	+ 46	35.0	13
477	513	+ 8	36.7	7
752	749	0	44.3	6
1508	1428	- 5	30.5	2
2373	2240	- 6	48.5	2
3857	3627	- 6	53.8	1
5078	4777	- 6	115.0	2
6417	6021	- 6	131.6	2

TABLE V

Summary of LACS Contractor (Rockwell) Analyses
of Blind Sulfate QC Samples

<u>Sample $\mu\text{g SO}_4$</u>	<u>RISC Mean ($\mu\text{g SO}_4$)</u>	<u>% Difference</u>	<u>σ</u>	<u>$100\sigma/\text{RISC Mean}$</u>
121	109	- 10	5.5	5
350	320	- 9	13.4	4
804	732	- 9	34.3	5
1262	1145	- 9	59.7	5
1811	1626	- 10	91.1	6

A set of eight quality assurance guidelines was prepared for the Office of Mobile Source Air Pollution Control. Guidelines and test procedure documents were developed for the following engine categories: (1) light-duty gasoline powered vehicles, (2) heavy-duty diesel engines, (3) light-duty diesel powered vehicles, and (4) heavy duty gasoline engines. These guidelines and test procedures are available in one document entitled "Guidelines for Quality Assurance Program for Mobile Source Emission Measurement Systems."

In order to assess the impact of pollutant emissions from catalyst-equipped vehicles on the ambient air adjacent to a freeway in Southern California, a variety of pollutants are being monitored under the LACS program by both integrated and continuous methods. The study site composition is shown in Figure 2.

Six integrating sampling methodologies are in use. The high volume sampler (hi-vol), using a 20x25 cm glass fiber filter, analyzed for: total suspended particulates (TSP), water soluble sulfates ($\text{SO}_4^{=}$), water soluble nitrates (NO_3^{+}), ammonium ion (NH_4^{+}), and lead (Pb) by standard wet chemical analysis techniques. Summary graphs of the upwind (Site A), downwind (SITE C), and difference (C minus A) $\text{SO}_4^{=}$ and Pb data obtained during the 1500-1900 hours evening rush hour are shown in Figures 3 and 4.

Samples obtained from membrane samplers, using a 102 mm circular filter, are analyzed for TSP, SO_4 , NO_2 , and NH_4^{+} by wet chemistry, plus 9 selected elements by x-ray fluorescence (XRF). The elements are sulfur (S), lead (Pb), aluminum (Al), silicon (Si), calcium (Ca), chlorine (Cl), iron (Fe), zinc (Zn), and bromine (Br).

Andersen cascade Impactors, using five impactor stages made of aluminum for aerosol size fractionation and backup filters (102 mm in diameter) for an additional size fraction are used. Analyses on the backup filter are by the same techniques listed for membrane samplers.

Dichotomous samplers, using 3 Teflon filters (37 mm in diameter) give aerosol size fraction information in 3 ranges by a nonimpaction method. Analyses on all filters are for $\text{SO}_4^{=}$, NH_4^{+} , strong acidity, and the same 9 elements as obtained with the membrane samplers.

Sulfur dioxide bubblers are analyzed by the standard Federal Reference Method.

Experimental high flowrate aerosol samplers using 2 impactor stages and an electrostatic precipitator to obtain size fraction information in 3 ranges with daily aerosol collection in gram quantities for subsequent exploratory compound identification analyses.

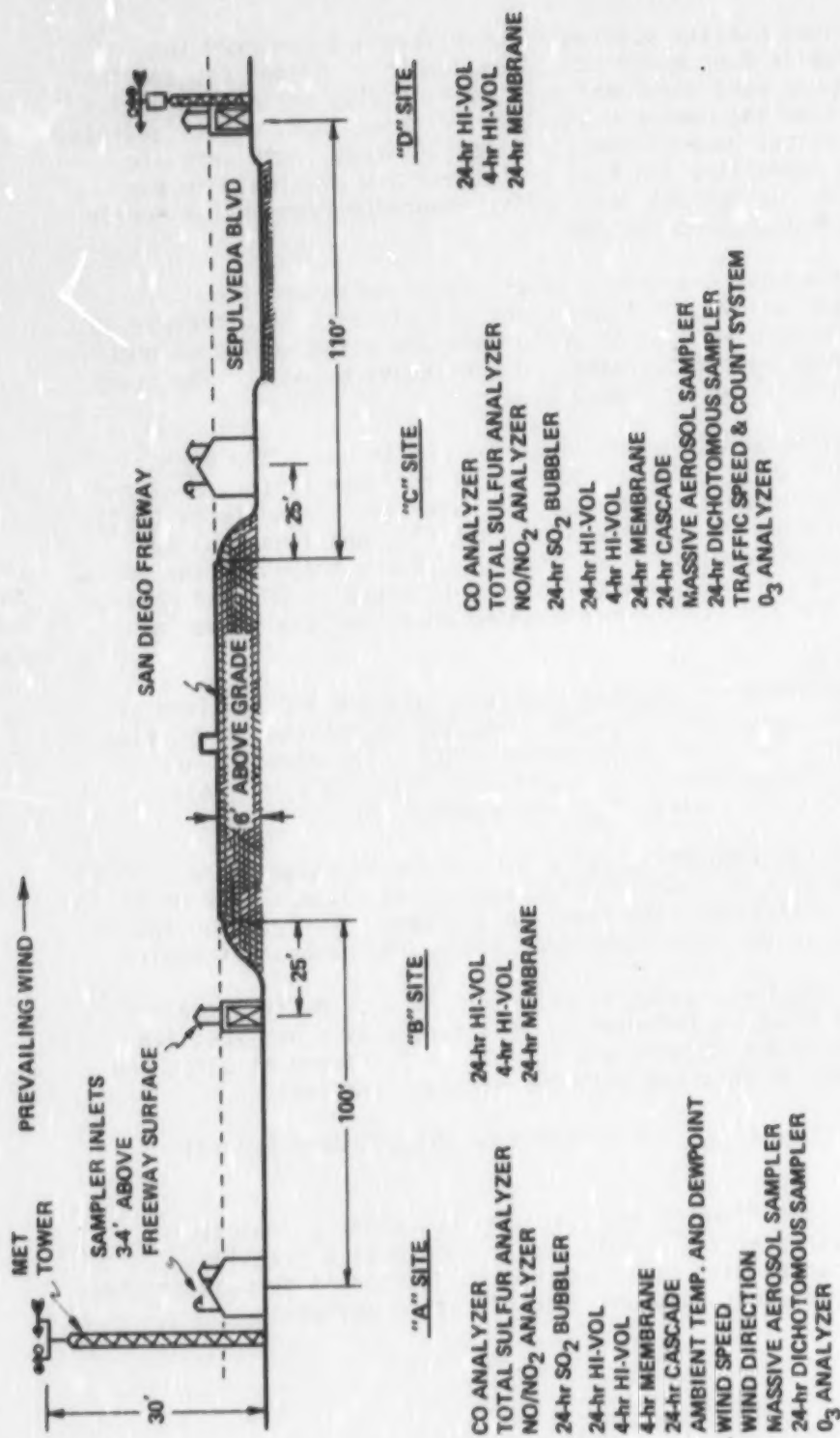


Figure 2. LACS Study Site Composition and Elevation

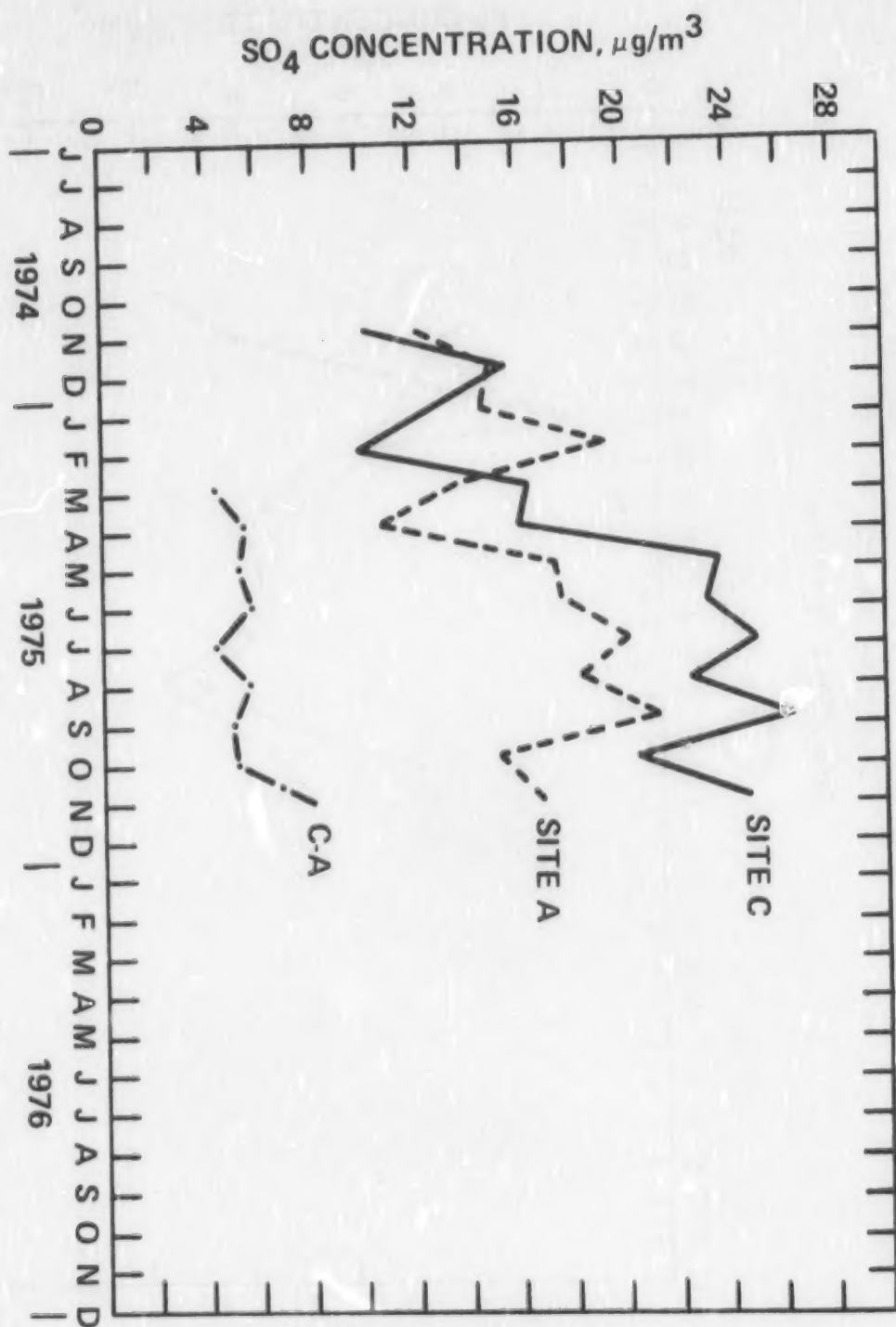


Figure 3. LACS Data
 Hi-Vol Sulfates (SO₄)
 Monthly Averages of 1500–1900 Hour Data

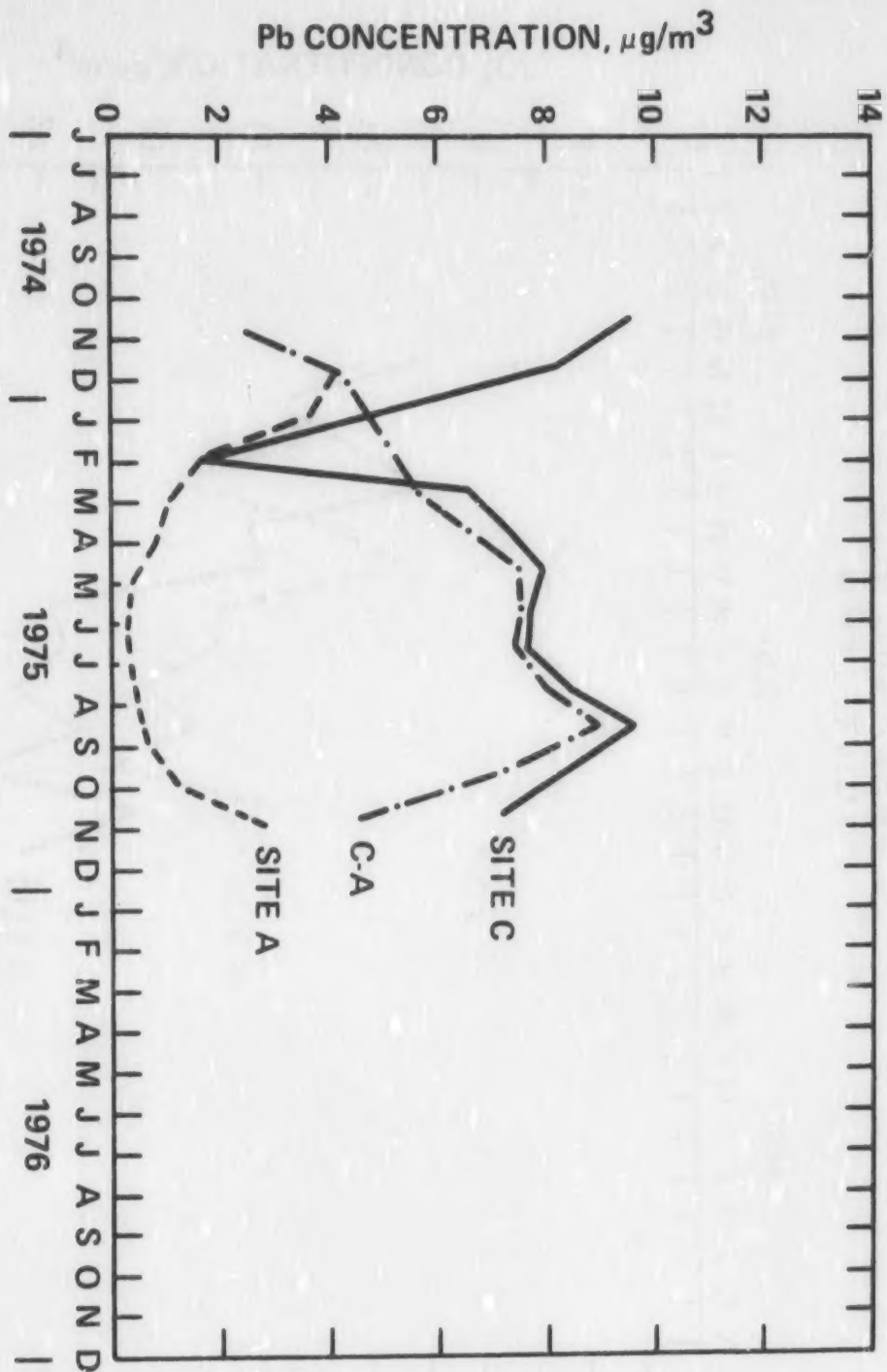


Figure 4. LACS Data
 Hi-Vol Lead (Pb)
 Monthly Averages of 1500-1900 Hour Data

Pollutants monitored by continuous methods are: carbon monoxide (CO) by infrared spectroscopy; nitric oxide (NO) and nitrogen (NO₂) by chemiluminescence with ozone; and total sulfur in the gas phase by flame photometric analyses. The dramatic cross-freeway difference for CO during the evening rush hour is illustrated by the graph in Figure 5.

Associated measurements are also carried out: ambient temperature and ambient dewpoint; wind speed and wind direction using sensors at the 10 meter level; and installation of a system to monitor traffic speed and count is in progress.

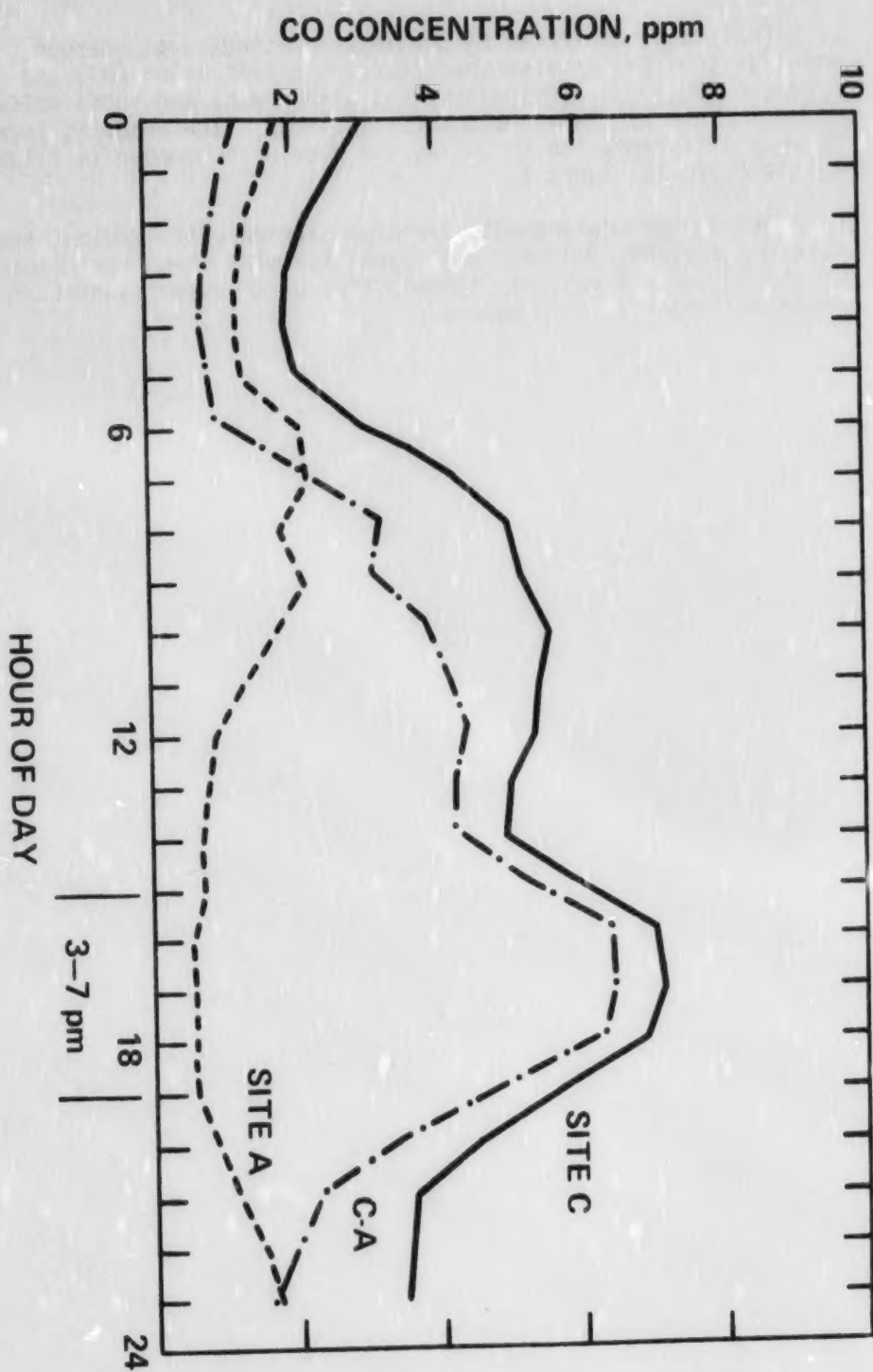


Figure 5. LACS Data
5/75
Carbon Monoxide (CO) by Hour

B. Environmental Sciences Research Laboratory/Research Triangle Park

This report covers work done in the Environmental Sciences Research Laboratory on the catalyst program from approximately the second quarter of FY 75 to the third quarter of FY 76. Research was conducted in four major areas: emissions measurement and characterization, atmospheric chemistry, ambient air measurement techniques, and modeling.

All of the activity in the emissions measurement and characterization area was geared to support the Administrator's intention to promulgate in the spring of 1976 a sulfate emission standard for light-duty vehicles. This work, which is reported in detail in Supplement III (Appendix B), involved further development of emissions measurement techniques and the establishment of baseline sulfate emission data. The effect of vehicle type and of operating mode on sulfate emissions was studied. This work was coordinated with related work being done at the EPA Mobile Source Air Pollution Control Laboratory in Ann Arbor, Michigan. A summary of sulfate emissions data under various operating conditions is given in Table VI.

The development of techniques and instrumentation to measure sulfuric acid and other sulfate aerosols in roadways and in the immediate vicinity of roadways has always been an important part of the catalyst program. (It is also important to other programs, such as the control of sulfur oxides from stationary sources.) To obtain information on the variety of sulfate species that could be present, measurement techniques have been developed for sulfuric acid, strong acid, particulate sulfur, water soluble sulfate, ammonium, and metals. Figure 6 shows a schematic design of a newly developed automatic sulfuric acid monitor. These techniques would be applied to a sample which would be collected in such a way so as to preserve its chemical and physical integrity during collection and storage prior to analysis. The dichotomous sampler, which was developed to separate particles into two size fractions during collection, is being used for this purpose.

An invitation was given to the U.S. Environmental Protection Agency (EPA) by General Motors (GM) to participate in a test track study at the GM Proving Ground to measure the effect on air quality of emissions from a fleet of catalyst-equipped vehicles under controlled experimental conditions. The test fleet consisted of 352 low-mileage 1975 and 1976 catalyst-equipped vehicles with air pumps provided by manufacturers. During October 1975 for about two hours a day, 350 vehicles were operated in packs on four lanes at a speed of 50 miles per hour. This mode of operation was equivalent to a traffic density of 5,460 vehicles an hour. The fuel used contained 0.03 weight percent sulfur; eight vehicles were equipped by GM to emit sulfur hexafluoride as a tracer. A vehicle was equipped by EPA to measure particle sizes, sulfate, and sulfuric acid

TABLE VI

SO₄ Emissions - 1975-1976 Catalyst Cars
(mg/mile)

Category	No. of Cars	Fuel	Crowded Freeway Simul.	Urban Simul.	Highway Simul.
'75-'76 California production cars (Olson study)	101	tank fuel 0.03% S average	15.8	4.4	22.6
'75 49-state production cars (baseline study)	11	0.03% S	14.9	7.9	19.8
'76 production Mavericks (baseline study)	5	0.03% S	34.7 ± 6.7	13.3 ± 6.0	41.4 ± 8.3
'76, 49-state (ESRL fuel study)	6	0.02% S	NA	1.6	5.8
		0.041% S	NA	3.7	15.4
		0.059% S	NA	5.5	20.9
		0.084% S	NA	12.0	49.5
Prototype air-pump cars (Exxon study)	6	0.019% S	NA	50.8	31.9 (40 mph SS)

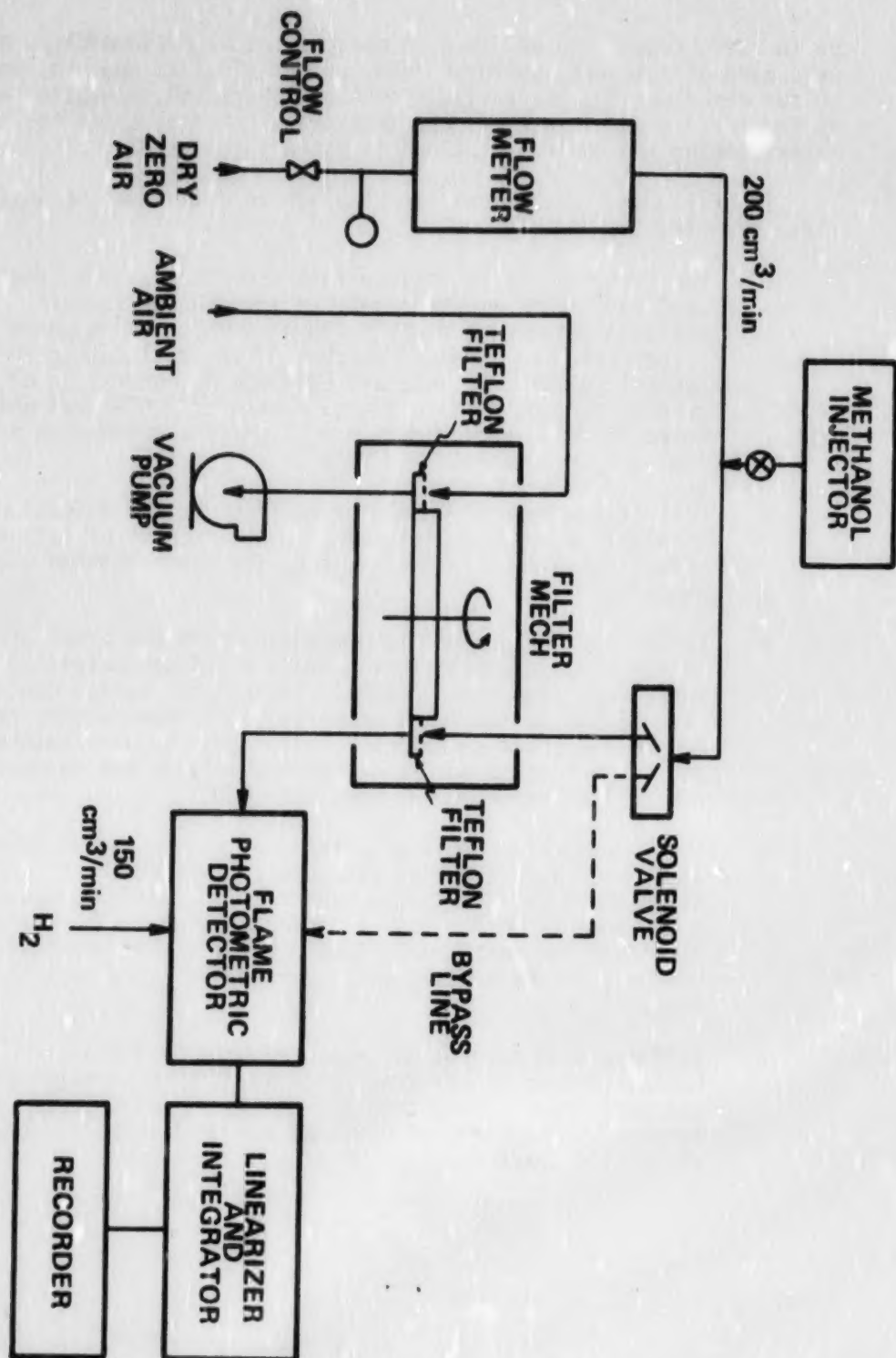


Figure 6. Schematic Diagram of Sulfuric Acid Monitor.

on the test track. In addition to meteorological measurements, measurements were made of sulfates, sulfuric acid, sulfur dioxide, ammonia, ammonium, sulfur hexafluoride, and particle size at towers and in mobile laboratories at several distances just off the test track. A diagram of the test track showing monitoring locations is given in Figure 7.

The following conclusions can be drawn to date from the analysis of these experiments.

- The flow rate of aerosol sulfate from the vehicle fleet was measured by an EPA grantee. The average sulfate emission rate per car was 0.018 g/mi which corresponds to a conversion of about 12 percent of the fuel sulfur to aerosol sulfate. A separate estimate by General Motors gave an average sulfate emission rate of 0.037 g/mi which corresponds to approximately a 27 percent conversion of fuel sulfur to aerosol sulfate.
- Most of the aerosol mass emitted from the air injection catalyst-equipped vehicles was in the form of ultrafine sulfur-containing aerosol in the size range between 0.01 and 0.1 μm .
- During the background measurements before and after operation of the vehicle fleet, this ultrafine sulfur-containing aerosol was almost completely absent. Instead the sulfur-containing aerosol was in the usual urban-regional fine aerosol range of 0.1 to 1 μm particle sizes. This "aged" sulfur-containing aerosol was not acid, so it was probably in the form of neutralized ammonium sulfate.
- The ultrafine aerosols grow into the size range of "aged" aerosols. When the wind was across the test track (shorter aging time) most of the aerosol from the vehicles measured 30 m off the test track was ultrafine aerosol. When the wind blew down the test track (longer aging time) one-third to one-half of the aerosol shifted into the "aged" 0.1 to 1 μm range.
- Sulfuric acid aerosol was measured both inside a moving vehicle and at an off-track site about 20 m downwind of the test track. More than two-thirds of the sulfate emitted by the fleet of cars was measured as sulfuric acid at the off-track site.

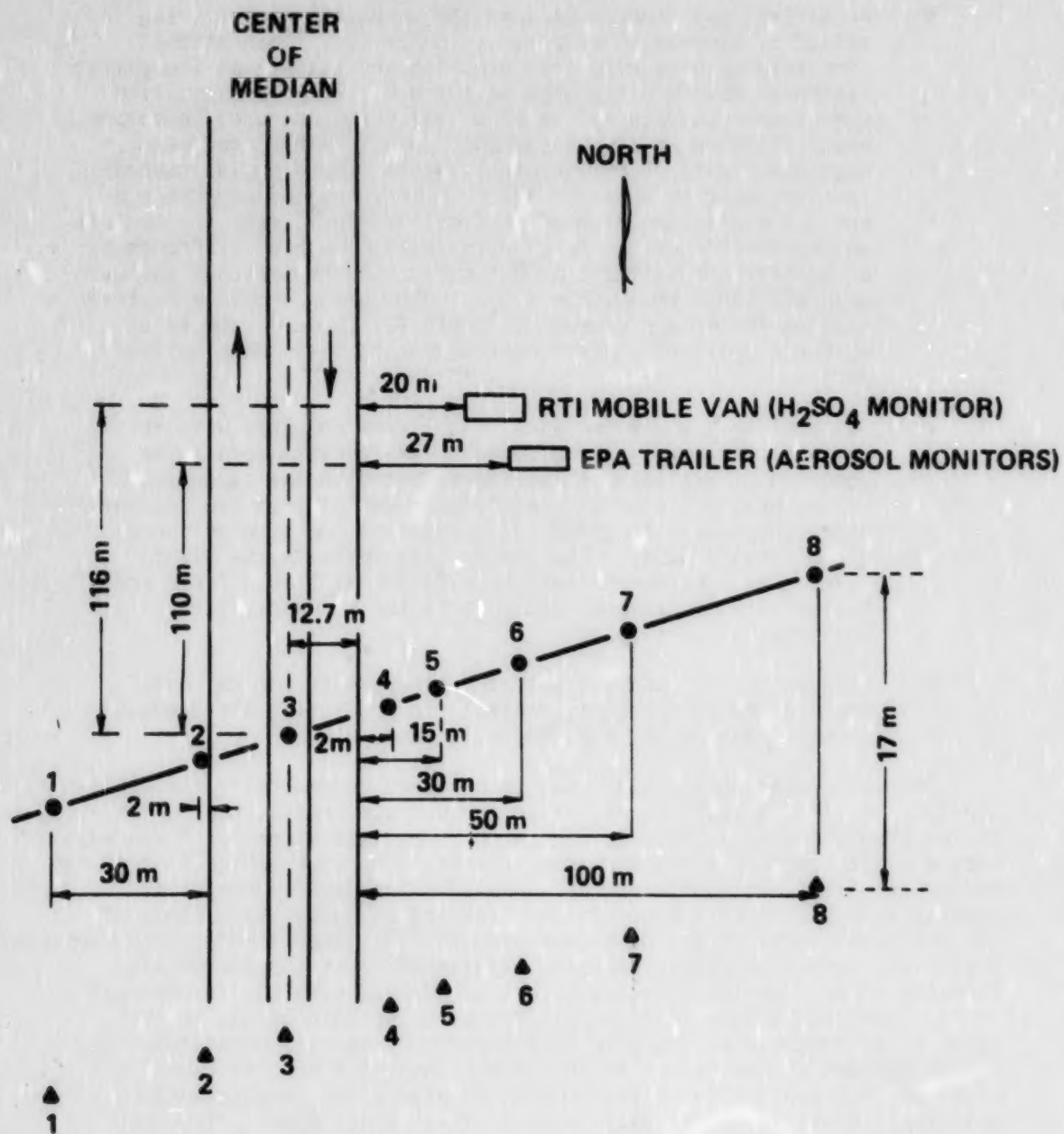


Figure 7. Location of EPA Dichotomous Samplers (Circles), General Motors Sampling Towers (Triangles), and Mobile Laboratories at General Motors Milford Proving Ground, October 1975.

- An attempt was made to measure the potential neutralizing effect of ammonia on sulfuric acid aerosol. This attempt consisted of measuring both ammonium and sulfate at increasing distances downwind from the test track. In most cases, the ammonium-to-sulfate ratios essentially corresponded to complete neutralization at all measurement points rather than being consistent with gradual neutralization. Apparently, neutralization occurred as an artifact during sampling and storage and not during the transport of sulfuric acid from the vehicles on the test track to the sampling sites. Other measurements of acidity and sulfuric acid indicate the presence of sulfuric acid off the roadway, but suggest partial or complete neutralization 100 meters downwind. Table VII shows a summary of sulfuric acid and sulfate results during selected sampling periods.
- Computations by the EPA HIWAY model were compared with the sulfate concentrations reported by GM investigators. The computed values were in good agreement with the experimental values when the wind was nearly perpendicular to the roadway under unstable meteorological conditions and at wind speeds at or above 1 m/sec. The tracer data indicate the HIWAY model tends to overestimate by a factor of 2 to 3 for E and F stability conditions, and by a factor of nearly 2 for the parallel wind case.
- Neither the off-roadway sulfate measurements nor the model results are likely to be accurate in predicting the commuter exposure during the parallel wind case.

Modeling research now under way is designed to determine the applicability of the EPA HIWAY model, or an appropriate modification of it, to the prediction of sulfate levels in the immediate vicinity of roadways. Work was also done on point and area sources. The work, which is reported in greater detail in Supplement III, includes the development of a roadway data base from a study in New York and an analysis in terms of the EPA HIWAY model of the data generated in "The General Motors/Environmental Protection Agency Sulfate Dispersion Experiment." The supplement also includes a paper on the modeling effort associated with this experiment. It is important to note that overprediction of sulfate levels in the vicinity of roadways as found in this experiment is not unexpected. It was recognized at the outset of this experiment that the EPA HIWAY model was not applicable to the problem of predicting vehicle-emitted pollutant levels in the roadway or very close to it, especially under very low wind speed conditions. The effort was nevertheless made to determine if the model could be adapted to this situation or if it would suggest a route to the development of an appropriate highway model.

TABLE VII

Comparison of Sulfuric Acid and Sulfate Results

Date	Wind Direction	Wind Speed km/h	Background Sulfate (BS) ₃ $\mu\text{g}/\text{m}^3$	Downwind Sulfate (DS) ₃ $\mu\text{g}/\text{m}^3$	$\Delta\text{SO}_4 = (\text{DS} - \text{BS})$ $\mu\text{g}/\text{m}^3$	$\text{H}_2\text{SO}_4/\Delta\text{SO}_4 =$
10/1/75	285°	15	2.75	4.51	1.76	1.08
10/2/75	330°	13	0.59	3.49	2.90	0.38
10/3/75	335°	8	2.27	5.53	3.26	0.83
10/10/75	245°	6	17.19	20.65	3.46	1.56
10/13/75	195°	12	7.55	10.85	3.30	0.73

In late 1975, investigators under an EPA contract began a study in California to determine if sulfate emissions from 100 in-use catalyst-equipped vehicles are similar to or different than emissions from new, well-tuned vehicles. Plans call for three emission tests per year (at approximately 4,000-mile intervals) on these consumer owned and operated vehicles. Preliminary results, after one test interval, show that sulfate emissions from vehicles designed to meet California standards averaged 0.016 g/mi. This figure is considerably less than the average of 0.035 g/mi measured in the GM study and by dynamometer tests.

C. Health Effects Research Laboratory/Cincinnati

In fiscal year 74, the Environmental Toxicology Division, HERL, Cincinnati was instructed to reprogram its research effort and develop a program for comprehensive toxicologic assessment of emissions from automotive engines with oxidative catalytic converters in the exhaust train. The research effort was divided into two major segments, i.e., the assessment of biological effects in animals exposed to (A) whole emissions from engines with and without the catalyst and (B) single pollutants (noble metals and sulfates) associated with catalyst emissions.

Part A: Automotive Emission Studies with and without Catalytic Converters

The research program for the Toxicological Assessment of Mobile Emissions (TAME) is summarized in Table VIII. Basically, the program was designed to determine biological effects following subacute (7 days) and longer term inhalation exposures to irradiated (I) and nonirradiated (NI) catalytic and non-catalytic-treated emissions. Clean Air controls (CA) and pertinent sulfuric acid (H_2SO_4) exposures were made where appropriate. This report contains data from TAME M, N., and O studies. Data from the earlier TAME studies (I, J, K, L) are contained in the first Annual Catalyst Research Program Report and in the open literature.

A comparison of the biological data from the subacute studies indicated that when the catalyst was removed extensive histopathological lesions were found in adult animals and a significant mortality rate was observed in suckling rats. In the studies using catalyst-treated exhaust no biological changes were found which could be related to the increased sulfate emissions. The catalyst effectively reduced carbon monoxide (CO) and hydrocarbons (HC) in the exhaust which apparently had an effect (at least in a closed exposure system) on oxidant and nitrogen dioxide (NO_2) levels by altering the HC/ NO_x ratio. There was a resultant reduction in biological effects due to the exposure. The catalyst altered the type of particulate to one which contained sulfuric acid as a major component.

In the TAME-L study, experimental animals (rats and hamsters) were exposed for periods up to one month to the catalyst-treated exhaust. Lung tissues examined by light microscopy showed no detectable effects. The scanning electron microscopy examination did not reveal any changes in epithelial lining cells which could be related to the exposure or emitted sulfates. An additional investigation was undertaken to determine the effects of experimental animal chamber loading (species and numbers per inhalation chamber) and frequency of cage changes and chamber washing on the chamber ammonia build-up and its concomitant interaction with sulfuric acid. Data from this study served to improve experimental design of future studies related to investigation of sulfuric acid effect parameters.

TABLE VIII

Toxicological Assessment of the Mobile
Emissions (TAME) Studies

COMPARISON OF TEST CONDITIONS							
TAME STUDIES	I	J	K	L	M	N	O
Test period, days	7	7	7	32	88	39	38
Fuel	Ref.		Ref. + thiophene				
Engine	GM 73			75 Ford			
Catalyst	No	Beads			Monolith	No	
Exposures	NI I CA CO	NI I CA			NI I CA H ₂ SO ₄	NI I CA CO	

Studies on the physiological and pathological effects were conducted on TAME M, N, and O. Growth rate, pulmonary function and pulmonary pathology of young guinea pigs were examined following a 30-day continuous exposure to catalyst-treated and non-treated automobile emissions. Details of all TAME studies may be found in Supplement IV. Following exposures to the catalyst-treated emissions, there was some reduction in growth rate (0 to 20 percent). When catalytic equipment was removed, growth rate decreased (34 to 36 percent). Airway resistance in experimental animals was significantly greater (3 to 47 percent) in exhaust-exposed animals than clean air controls, and lung compliance was unchanged when the catalyst was used. However, removal of the catalyst resulted in an even larger increase in resistance (63 to 68 percent) accompanied by a significant decrease in compliance (35 to 39 percent), indicating bronchial constriction. Animals exposed to H_2SO_4 atmospheres which were similar in concentration and particle size to that found in catalytic emission atmospheres, showed a 3 percent decrease in growth rate, an 18 percent increase in resistance and no change in compliance when compared to clean air controls. Pulmonary lesions, as examined by light microscopy, were similar in incidence for all groups. However, those lesions seen in the lungs of animals exposed to emissions produced without catalytic equipment appeared more severe.

Behavioral studies indicated that exposure to both catalytic and non-catalytic-treated exhaust resulted in a significant reduction of spontaneous activity in rats. Blood gas analysis has shown that both H_2SO_4 and irradiated exhaust treated with a catalytic converter elicited a shift toward metabolic alkalosis during exposure. In contrast, exposure to carbon monoxide at levels comparable to that obtained in chambers without using a catalytic converter resulted in a shift of the blood toward acidity. The effects were less dramatic in the exhaust chamber without the converter, thereby indicating that other components of the non-catalyst exhaust tended to offset the action of the carbon monoxide. It should be emphasized that blood acid-base parameters returned to normal levels within one month after termination of all exposures.

In TAME M, lactating female rats and their newborn offspring were exposed to each of four treatment atmospheres (clean air, irradiated and nonirradiated catalytic exhaust, and H_2SO_4 mist). Tissues taken either from the lactating females sacrificed after 4 weeks' exposure to the catalyst-treated exhaust or from the weanling rats following 12 weeks' exposure showed no treatment effects. In both groups there was evidence of mild chronic respiratory disease. An increase in hemoglobin, hematocrit, and total erythrocyte count was observed in the young animals exposed to auto exhaust. The cause was not apparent but may be related to a mild hypoxia in these groups. There were no treatment-related effects upon body weight changes in either lactating females or their offspring. There was no treatment-related mortality.

Developmental and growth studies in which pregnant hamsters were exposed to irradiated exhaust using the catalytic system did not reveal any gross teratogenic defects or embryotoxicity. However, there was a slight delay in the onset of parturition. Postnatal growth in the catalytic exhaust atmosphere appeared normal with the exception of a

decreased ability to perform a postnatal reflex test (the "startle" reflex). H_2SO_4 aerosol maintained at the catalytic system level resulted in a slight delay in the onset of parturition with no other apparent effects. Non-catalytic exhaust environments were not tested.

Studies with developing chick embryos revealed increased embryonic mortality following exhaust exposure without the catalyst compared to exposure to catalyst-treated exhaust; at fourteen days, mortality was 12 to 39 percent with the catalytic system compared to 51 to 55 percent without the catalyst. The heart to body weight ratio increased 34 to 36 percent in the exhaust chambers without the catalytic system, but only 0 to 12 percent with the catalyst. Embryonic body weight decreased 6 to 36 percent with the catalytic system and 13 to 26 percent without it. The liver to body weight ratio increased as much as 21 percent in both catalyst and non-catalyst systems. H_2SO_4 aerosol maintained at the catalytic emission level resulted in a slight increase in mortality accompanied by a 17 percent decrease in body weight but with no other apparent effects. Carbon monoxide maintained at the non-catalytic emission level resulted in a mortality of 30 percent, a decrease in embryonic body weight of 22 percent, an increase in the heart to body weight ratio of 28 percent, and an increase in the spleen to body weight ratio of 37 percent.

Selected biochemical and clinical health indicators in general showed that the use of the catalyst decreased the detrimental effects of engine exhaust. Hematocrit, serum lactic dehydrogenase (LDH), glutamic-oxalacetic transaminase (GOT) and lysozymes were measured in groups of rats exposed to diluted emissions from an automobile engine with and without catalyst; to sulfuric acid; or to carbon monoxide alone at a level comparable to that in the automotive exhaust. An elevation in hematocrit was observed in the animals exposed to exhaust gas without the catalyst and in those exposed to carbon monoxide. Serum lactic dehydrogenase activity was elevated in the groups of rats in the experiment conducted without the catalyst, but no alteration was observed in the animals from the experiment utilizing the catalyst, or in those exposed to carbon monoxide alone. Measurements indicated that the observed elevation of hemoglobin and hematocrit was due to polycythemia and not to dehydration. Catalytic exhaust emissions resulted in slightly increased serum triglycerides while serum cholesterol was not affected.

Examination of specific parameters of lipid and carbohydrate catabolism such as the oxidation of ^{14}C -1-palmitic acid to $^{14}CO_2$ to represent lipid catabolism and the oxidation of ^{14}C -U-glucose to represent the breakdown of carbohydrate, revealed definite changes only in animals maintained on a special diet containing reduced levels of Cu and Zn. The rats receiving this special diet demonstrated decreased glucose oxidation rates following exposure to both non-irradiated and catalytically altered exhaust. The animals maintained on commercial rat chow did not show any treatment effect in their ability to oxidize glucose in TAME N and O. The CO exposed animals in TAME O exhibited a decreased (15 percent) ability to oxidize palmitate, as compared with the other groups.

Preliminary results from tissue culture experiments demonstrated that non-catalytic treated exhaust emissions were approximately 35 percent more toxic when compared with catalytic-treated exhaust. In addition, sulfuric acid levels equivalent to the titratable acidity present in the catalytic exhaust had no effect.

Functional integrity of the pulmonary aryl hydrocarbon hydroxylase (PAHH) was studied because of its possible role in biotransformation of hydrocarbons. In previous TAME studies, it was shown that exposure to non-catalyst-modified auto exhaust markedly depressed specific PAHH activity. There was a lesser but still significant depression of PAHH along with increased relative lung mass after exposure to catalyst-modified irradiated exhaust. In the TAME M study, pregnant hamsters and their offspring were continuously exposed and the determinations of total PAHH activity and relative lung mass (lung to body weight ratio) were made in post-weanling hamsters. Body and lung weights were greater in the sulfuric acid (S) and irradiated exhaust exposure (I) groups; as a result, relative lung mass was not significantly different. Specific PAHH activity was not different from controls in the sulfuric acid-exposed group. In the irradiated exhaust-exposed group it was depressed by about 9 percent; this depression was consistent with the pattern in previous studies.

For TAME studies M, N, and O, a 1975 Ford 400 CID California production engine equipped with two oxidative catalytic converters was operated continuously (24 hr/day) on an engine dynamometer test stand using the California cycle. Both TAME M and TAME N utilized new engines and new catalysts; in TAME O the catalytic converters were removed. In TAME M, Engelhard Pt/Pd catalysts with American Lava monolith substrate were used and in TAME N an identical catalyst formulation with a substrate made by Corning was substituted. The fuel used was unleaded 91 octane indolene with thiophene added to produce a high sulfur fuel (0.10 percent S by weight).

Comparison of the atmospheres in the exposure chambers and the dilution tube generated with and without the use of catalytic converter produced the following results: (1) Major decreases in concentrations of carbon monoxide (90 percent) and total hydrocarbons (70 percent) occurred with the use of the catalytic converter in the exhaust system. (2) The use of a converter caused a large decrease in sulfur dioxide (45 percent), but a resultant increase of sulfuric acid droplets with a mass median diameter of less than $0.3\ \mu\text{m}$. (3) A significant decrease in the oxidative capacity of the catalyst occurred with use (TAME M, 45,000 miles) with a resultant increase in carbon monoxide levels and a decrease in total particulate. The sulfate mass decreased approximately 80 percent during the course of the study. In the shorter-duration TAME N study (39 days or 20,000 miles) only a slight CO increase resulted and sulfate decreased 24 percent. Special procedures were followed to prevent carburetor enrichment and possible catalyst overloading.

The results of the Toxicological Assessment of Mobile Emissions (TAME) studies have demonstrated that the toxicological effects of automobile emissions are ameliorated to a considerable degree by the addition of a catalyst.

- Pulmonary function, mortality and heart weight/body weight ratios of chick embryos, serum enzyme levels, enzyme activity, tissue metabolism, and histopathology studies have shown that addition of the catalyst resulted in decreased biological damage.
- Sulfuric acid exposures at levels comparable to that produced by the catalyst produced few effects.
- Single pollutant studies suggested that platinum and palladium were relatively harmless at predicted emission levels. Platinum is rapidly excreted while palladium, although quite toxic, is apparently only slightly absorbed when given by intragastric route at low levels.
- It was noted that there was a decrease in the oxidative capacity of the catalyst as miles accumulated, which resulted in marked decreases in sulfuric acid and sulfate emissions.
- Finally, it is realized that additional data concerned with other catalytic systems and emission products are needed. Additional studies were proposed for FY 76 and 77.

PART B: Toxicologic Study of Auto Exhaust Catalyst Components

The second part (B) of the document presents biological findings on the single pollutants related to catalyst emission studies. Earlier data dealing with individual products of catalyst emissions were reported in the first Annual Catalyst Research Program Report and in the open literature. The present data include results of the continuation of the studies of noble metals (Pt and Pd), sulfuric acid and sulfates, environmental chelates, and ozone (Supplement IV).

Whole body retention, excretion, lung clearance, distribution and concentration of radioactive platinum (^{191}Pt) in other tissues was determined in rats following a single inhalation exposure to different chemical forms of ^{191}Pt . The chemical forms of ^{191}Pt used in this study were $^{191}\text{PtCl}_4$, $^{191}\text{Pt}(\text{SO}_4)_2$, ^{191}PtO , and ^{191}Pt metal. Immediately after exposure most of the ^{191}Pt was found in the gastrointestinal and respiratory tract. Movement of the ^{191}Pt through the gastrointestinal tract was rapid, most of it was eliminated within 24 hours after exposure. Lung clearance was much slower with a half-time of about 8 days. In addition to the lungs, kidney and bone contained the highest concentrations of ^{191}Pt . Summary of lung retention data is shown in Table IX.

TABLE IX

Percent of Initial Lung Burden of Platinum Retained with Time
in the Lungs of Rats

Day	CHEMICAL FORM		
	Pt Metal	PtO	Pt(SO ₄) ₂
1	63.0	57.2	73.7
2	49.5	60.9	43.4
4	41.3	49.0	20.4
8	42.9	28.6	--
16	28.0	17.9	4.4

Palladium sulfate markedly affected the incorporation of L-(3,4-³H₂)-proline into non-dialyzable fractions in 10-day chick embryo cartilage explants with a 55 to 65 percent reduction in uptake in a substrate concentration range of 0.06-0.6mM. Under these conditions the synthesis of ³H-hydroxyproline was almost completely inhibited. Experiments with prolyl hydroxylase indicated a strong irreversible inhibition of the enzyme with a competition between iron and palladium at the active site of prolyl hydroxylase. This finding suggests a potential mechanism of palladium toxicity.

The toxicity to pulmonary free cells (PFC) of sulfuric acid (H₂SO₄) and palladium sulfate (PdSO₄) administered intratracheally was investigated in rats. The amount of H₂SO₄ solution administered was 0.45 mg SO₄/kg body weight. The aqueous solution of hydrous PdSO₄ solution was given at a SO₄ dose rate equivalent to that of the H₂SO₄ group and a Pd dose of 0.5 mg/kg. Twenty-four hours after dosing, the PFC were collected by saline endobronchial lavage. The following significant treatment effects were found in the PdSO₄ group: increased total numbers of free cells, including both viable and nonviable nucleated cells, phagocytic and nonphagocytic macrophages, polymorphonuclear leukocytes, and red blood cells; increased number of cells with test spheres; increased dried lung mass. No such effects were found in the H₂SO₄ exposed group. There were no apparent effects on percentage of nonviable cells, on proportional phagocytic activity, or on cell size in either group.

The effect of Pt, Pd, Mg, Mn, Ca, Ce, Na, and NH₄ sulfates upon succinate-dependent respiration was tested in rat liver slices and homogenates. Cadmium, a known potent inhibitor of the mitochondrial respiratory chain, was used in this experiment as a reference toxicant. The results indicated that the sulfate ion in tissue slices or in a homogenate did not affect the respiratory chain. Cadmium appeared to be the most potent cation inhibiting O₂ uptake by approximately 50 percent as 2 x 10⁻⁵ M and 100 percent at 3.3 x 10⁻⁵ M. To achieve a 50 percent inhibition by PdSO₄ more than 10⁻³ M was required. Pt appeared to be slightly more toxic than Pd under the same experimental conditions. Other cations (Mn, Mg, Ca) were not inhibitory at concentrations up to 10⁻³ M and even appeared to have a slight stimulatory effect. No effects could be demonstrated with low concentration of Na or NH₄ ions. Intragastric administration of a single dose and of multiple doses of CdSO₄, Pt(SO₄)₂, and PdSO₄ at 8 and 80 μmole per kg body weight, did not affect succinate-dependent respiration in any of the organ tissues tested (kidney, liver, heart, and lung). It is probable that under the experimental conditions these metals were not absorbed in amounts sufficient to cause any effect on the mitochondrial respiration of soft tissue organs. The *in vitro* experiment suggests that Cd should have impaired this enzyme system if absorbed in significant quantity and accumulated in the tested organs.

Products from the combustion of tobacco, gasoline, and coal from other pyrolytic processes are ubiquitous sources of metal binding agents which may react with trace metals thus altering essential biological functions. The ability of the catalyst and non-catalyst, as well as catalytically and non-catalytically-treated auto exhaust condensate to bind copper was demonstrated. It was shown further that the ability of these condensates to bind copper was greater than their ability to bind zinc, cadmium, iron, and lead. In preliminary enzyme activity studies, it was shown that catalytically-altered auto exhaust concentrate showed a greater inhibition of tyrosinase (a copper-dependent enzyme) than non-catalytically-treated exhaust.

The metabolic response of lung tissue to ozone was studied in rats and monkeys after exposure of animals to various levels of ozone (0.1 to 0.8 ppm) for 1 to 30 days. In rats, 0.8 ppm ozone exposure resulted in a 40 to 50 percent increase in oxygen utilization by lung homogenates. Activities of marker enzymes, such as mitochondrial succinate-cytochrome c reductase, microsomal NADPH-cytochrome c reductase and cytosolic glucose-6-phosphate dehydrogenase, increased 40 to 70 percent over control after 3 to 4 days of exposure, and remained elevated throughout the continuous exposure for 30 days. In monkeys, the observations were similar except that the magnitude of biochemical changes was relatively smaller. Exposure of animals to lower levels of ozone resulted in proportionately smaller biochemical changes in the lung, with detectable effects down to 0.2 ppm. With dietary deficiency of vitamin E, ozone changes were detected at 0.01 ppm.

D. Health Effects Research Laboratory/Research Triangle Park, N.C.

Research which is part of the Catalyst Research Program (CRP) under way in the Health Effects Research Laboratory at RTP may be described as falling generally in three categories: studies of trace metals associated with catalyst-equipped vehicles (focusing primarily on platinum compounds), sulfate studies (focusing primarily on sulfuric acid), and a study of emissions from consumer-owned catalyst-equipped vehicles designed to meet Federal emissions standards. There are also other related studies such as evaluation of in vitro screening systems which appear promising as health effects indicators for both the pollutants associated with catalyst vehicles and other pollutants.

● Trace Metals Research

The trace metals portion of the CRP's research program has focused principally on platinum compounds, because this metal is commonly used in the noble metal oxidation catalyst employed by the U.S. automotive industry in reducing emissions to the level required by Federal law. The concern for health effects of platinum emissions differed from that for sulfuric acid in that it was not based upon known toxic effects of a pollutant characterized in exhaust emissions, but upon lack of knowledge about the toxicology of platinum compounds which might be emitted from catalyst-equipped vehicles.

Research on platinum included both development of measurement and emission characterization technology and also development of information on the toxicity of various platinum compounds which might be expected to be found in emissions from catalyst-equipped vehicles. Selection of platinum compounds for study in toxicity testing programs was based, in the absence of definitive data on a platinum component of automotive emissions, on prediction of those compounds most likely to be found in the particulate exhaust. These were platinum oxides and platinum sulfates.

The work in health related studies of platinum compounds has been under way for nearly two years and results to date have shown that toxicity of platinum compounds appears to be directly related to water solubility of these compounds. Since the platinum compounds most likely to be found in exhaust particulate are the insoluble oxides and the marginally soluble sulfates, concern for adverse health effects from platinum emissions is less now than at the initiation of the CRP. Table X summarizes the toxicity of various platinum compounds and other metal salts in the rat as a function of the route of exposure. Interest in pursuing platinum toxicology programs continues, however, for two basic reasons: long-term studies on carcinogenicity, mutagenicity, and cytotoxicity are not yet completed; preliminary findings show possible adverse effects from the platinum compounds being studied. Also, it has been shown that it is possible under laboratory conditions to methylate platinum via the same vitamin B₁₂ (methylcobalamin) reaction by which mercury is methylated.

TABLE X

Lethal Doses in the Rat of Various Metallic
Compounds After Intraperitoneal or Oral Administration

Compound	Route	Lethal Dose					
		(mmoles/kg)			(mg cation/kg)		
		LD ₁₀	LD ₅₀	LD ₉₀	LD ₁₀	LD ₅₀	LD ₉₀
MnCl ₂ ·4H ₂ O	ip	0.56	0.70	0.87	31	38	48
	oral	6.3	7.5	9.0	350	410	490
PbCl ₂	ip	1.6	8.5	16.8	330	1760	3500
PdCl ₂ ·2H ₂ O	ip	0.39	0.57	0.82	42	60	87
	oral	1.56	2.7	4.8	166	290	520
PdSO ₄	ip	--	1.42	1.8	--	151	125
PdCl ₂	ip	--	2.5	--	--	490	--
PtCl ₄	ip	--	0.11	--	--	22	--
	oral	0.31	0.70	1.57	60	136	310
Pt(SO ₄) ₂ ·4H ₂ O	ip	0.56	0.68	0.82	110	132	160
	ip	0.2- 0.3	0.3- 0.4	0.4- 0.6	39-59	59-78	78-117
	oral	1.37	2.2	3.5	270	430	690
RuCl ₃	oral	1.78	3.2	5.4	180	310	550

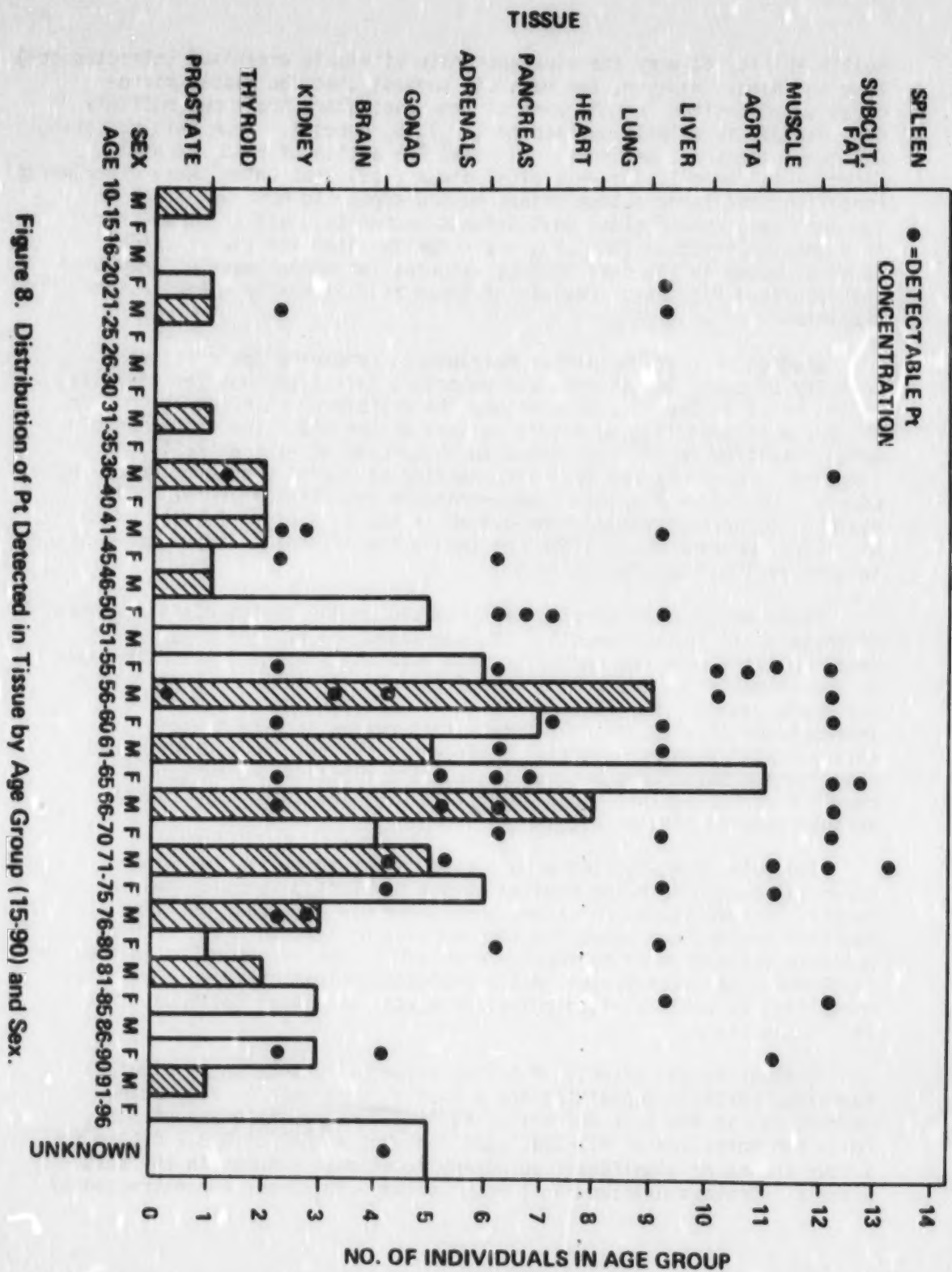
The biological activity of methylated platinum compounds thus formed has yet to be determined. The implications of disposal of platinum-containing automotive parts, as well as the emissions of platinum-containing exhaust particulate from catalyst-equipped vehicles for platinum uptake from soil to plants and possibly into the food-chain, is also a matter of concern to the Agency. As shown in Figure 8, platinum has been detected in human tissue although the significance of this finding is not presently known.

For the above two reasons -- lack of data on long-term effects of exposure and lack of information on platinum metabolites -- the CRP efforts in this area are important to continue. There are also some adverse effects being noted in preliminary data from other current studies as briefly described in the supplemental report on platinum research: platinum sulfate has been shown to be a moderate to severe eye irritant, and it may, at some concentrations, have an effect on behavior which could be characterized as depressant. Other data, preliminary at best, point to other possible adverse effects which must be carefully assessed before any final evaluation of the health effects of possible emissions of platinum compounds from catalyst-equipped vehicles can be made.

• Sulfate Research

The principal thrust of the sulfate toxicological research effort is to identify toxic agents via biological screening; to study the metabolic pathways and fate of toxic agents and identify target organs or tissues at risk; to study the mechanisms of damage and repair; and to develop dose response relationships. Although much ongoing research on the toxicology of sulfate compounds was not a formal part of the Catalyst Research Program and received support from other program areas, the results of the total sulfate research effort have a definite impact on assessing the hazard of catalyst emission products and are included here. Any output from these studies will be a contribution to construction of an improved spectrum of biological responses for use in epidemiological studies. The primary output will be animal dose response models which will serve as an input to the human dose response model.

Studies currently under way in HERL/RTP have provided significant toxicological information on the health effects of sulfur oxides. In-house investigations have continued to assess the toxicity of three different sulfur oxide substances on the clearance of both viable and non-viable particles deposited in the respiratory tract. The mucociliary clearance of radiolabelled killed streptococci was significantly reduced when mice were exposed to H_2SO_4 having a mass concentration of $160 \mu g/m^3$, although exposure to the other sulfur oxides [Na_2SO_4 , $(NH_4)_2SO_4$] had no effect on mucociliary clearance of these particles from the lungs or nose of mice. The inhalation of H_2SO_4 , $(NH_4)_2SO_4$, and Na_2SO_4 also failed to alter the rate of viable streptococci from the lungs of mice. The study indicated that neither H_2SO_4 nor Na_2SO_4 had any effect on the



host's ability to vary the clearance rate of viable organisms (streptococci) from the nose. However, the data did suggest that the viable micro-organisms deposited in this area of the respiratory tract may multiply more rapidly in animals exposed to $(\text{NH}_4)_2\text{SO}_4$ aerosol. From this research, the conclusions reached were: (1) that the action of H_2SO_4 aerosol might be on the ciliated epithelial airway; (2) that under these experimental conditions the three sulfur oxides tested appear to have no effect on the deep lung bactericidal host defense mechanisms; and (3) that there is a possibility that $(\text{NH}_4)_2\text{SO}_4$ may actually alter the bacteriocidal defense system in the nose of mice allowing for enhancement of growth of the deposited microbes. Details of these studies can be found in the supplement.

Studies on rabbit alveolar macrophages comparing the relative toxicity of metallic sulfates and chlorides indicated that the toxicity of the metal is the same with either the sulfate or chloride anion. On the basis of quantitative determinations of the molar concentration of metal resulting in net cell death in 50 percent of exposed cells as compared to controls the following ranking of toxicity was observed: $\text{Hg} > \text{Cd} > \text{V} > \text{Cu} > \text{Zn} > \text{Mn} > \text{Ni}$. Concentrations resulting in a net cell death of 50 percent ranged from 0.4 mM in the case of Hg to 3 mM with Ni. Zinc ammonium sulfate did not show a significantly different toxicity in this system from zinc sulfate.

Crude particulate samples being tested in the system contain several of these toxic trace elements. In some cases the net toxicity of the crude material does not correlate well with the predicted toxicity based on the summation of the toxicities of the metals contained within or on the crude sample. For this reason it is important to consider the interactions of toxic trace elements when evaluating the toxicity of environmental samples. Initial experiments designed to elucidate and quantitate interactions between toxic trace elements indicate that copper protects against vanadium cytotoxicity and selenium protects against cadmium cytotoxicity.

The role of H_2SO_4 (100 mg/m^3) as a co-carcinogen acting with a known carcinogen is being studied at the New York University Medical Center. In this study, which has been under way for about one year, hamsters are being exposed for long periods of time to H_2SO_4 with multiple intubation of benzo(a)pyrene (BaP). The report found in the supplement indicates typical daily exposure, weight changes, cumulative mortality, as well as histological data that have been collected thus far in the study.

A study on the effects of sulfur oxide pollutants on respiratory function, particle deposition and bronchial clearance is also being carried out at New York University Medical Center. Exposure of H_2SO_4 (mass concentration of $993\text{--}2991 \text{ } \mu\text{g/m}^3$) having a MMAD of $0.3 - 0.6 \text{ } \mu\text{m}$ for 1 hour showed no significant pulmonary functional changes in the test animals. Donkeys exposed for 1 hour to $(\text{NH}_4)_2\text{SO}_4$ (mass concentration of

121-1604 $\mu\text{g}/\text{m}^3$) having a MMAD of 0.2 - 0.6 μm did not significantly alter the bronchial clearance rate of inhaled ferric oxide aerosols (3 μg). Similarly, when donkeys were exposed to H_2SO_4 (mass concentration of 993-1364 $\mu\text{g}/\text{m}^3$) having a MMAD ranging from 0.3 - 0.6 μg for 1 hour and subsequently exposed to radiolabelled ferric oxide, no effect was evident on the initial pattern of deposition of the particle. However, preliminary data suggest that such exposure may significantly influence (slow) clearance of the deposited ferric oxide particle.

Research is under way at the Stanford Research Institute to determine the biological effects of exposure to H_2SO_4 on rats and guinea pigs. The animals were exposed to 110 mg/m^3 H_2SO_4 mist with MMD of 2.3 μm for 24 hours daily. The LD_{50} for rats was achieved in 37 days whereas the LD_{50} for guinea pigs, in the same environment, was achieved in about 3 hours. During these exposures, a variety of parameters were studied in the rat: body temperatures, weight and volume relationship of lungs, hematological evaluation, blood pH, respiratory gas analysis and plasma volume measurements. Guinea pigs were also exposed to 12.5 mg/m^3 of H_2SO_4 (MMD 2.0 μm). They developed an initial tachypnea which returned to normal the next day. No difference was seen in hematocrit nor in red cell counts. An interesting observation was that if the guinea pigs were able to survive an initial "shocking" concentration they were "tolerant" to much higher doses that would normally have been lethal.

Studies at IIT Research Institute (IITRI), Chicago, Illinois, have focused on the effects of single and multiple 3-hour inhalation exposures to varying concentrations of sulfuric acid mist in combination with 5 mg/m^3 of carbon particles on the mouse. As was true with acid mist alone, mice were more sensitive to acid mist and carbon particle mixtures (A-C) than hamsters. Only minimal mortality occurred among CF₁ mice after a single 3-hour exposure to 300 mg/m^3 or five daily 3-hour exposures to 200 mg/m^3 A-C. Three combinations of A-C concentration and exposure duration resulting in the same concentration-exposure time index (CI) were examined: 5 daily exposures at 3 hours each day to 200 mg/m^3 , 10 daily exposures to 100 mg/m^3 , and 20 daily exposures to 50 mg/m^3 A-C. Scanning electron microscopic (SEM) examination of nasal cavities, trachea, and lungs showed that the initial concentration of A-C is a more critical factor in tissue damage than the total number of exposures. Exposure to acid mist alone caused damage near the top and middle of the trachea, while the lower portion of the trachea was relatively free of damage and the lungs were normal. Addition of the 5 mg/m^3 carbon particulates to the acid mist extended the damage to the lower trachea and the bronchus of the lungs. The most severe changes, including emphysematous-like areas in the alveoli, were found in mice following five daily 3-hour exposures to 200 mg/m^3 A-C as shown in Figure 9. Histopathologic examination of these tissues did not disclose any marked changes, indicating the sensitivity of SEM in detecting tissue damage.

Infectivity studies conducted at the IITRI with various A-C concentrations demonstrated the following:

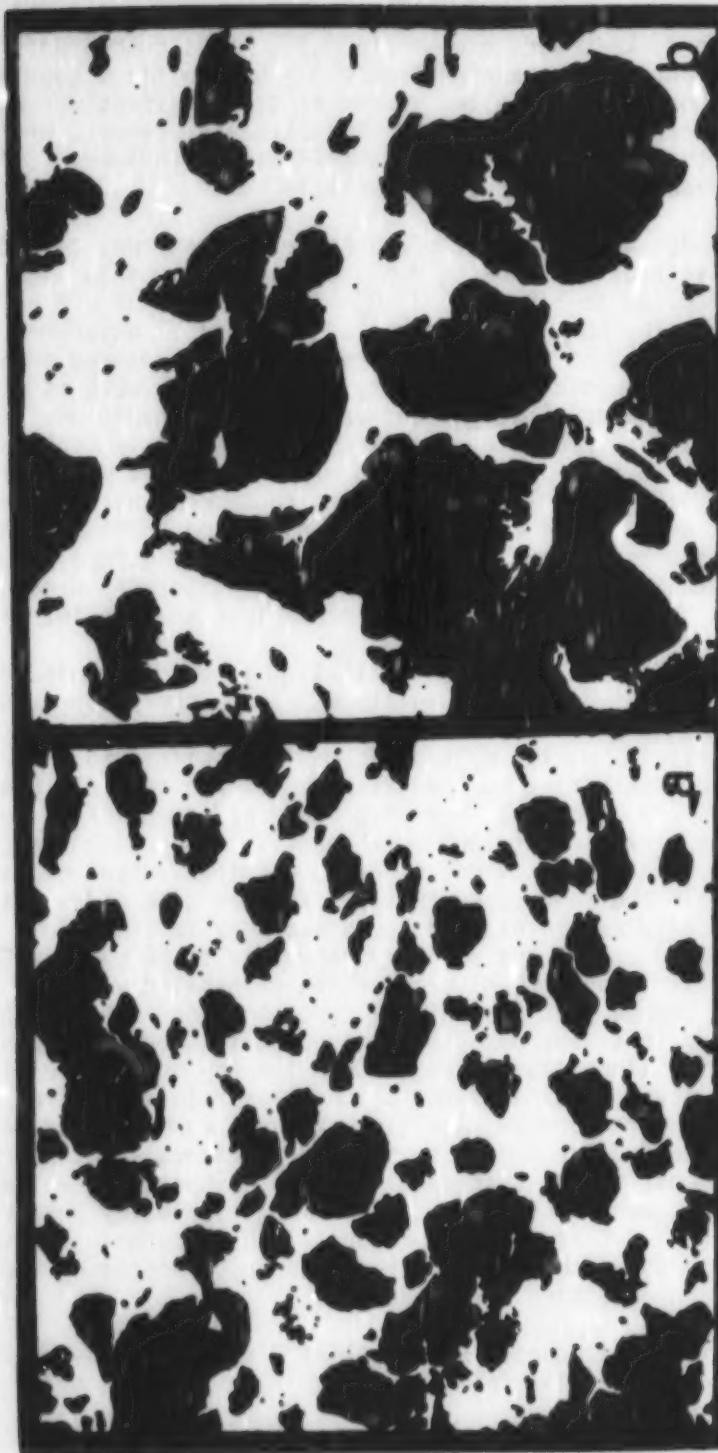


Figure 9. Lung of Mouse Exposed to Acid Mist-Carbon Particles Mixture: Thickened Alveolar Walls as well as Thin Filamentous Septa (a) 200X; (b) 550X.

- Increased mortalities occurred in hamsters after a single 6-hour exposure to 300 mg/m³ A-C or 48 hours after intranasal challenge with influenza virus.
- Five daily 3-hour exposures to 200 mg/m³ A-C immediately before or after challenge with a viral or bacterial agent significantly increased mortality rates of mice. A concurrent marked decrease in clearance rate of inhaled bacteria from the lungs was observed.
- Five, as well as ten daily 3-hour exposures 5 days/week to 100 mg/m³ A-C immediately after challenge with a bacterial agent also resulted in markedly increased mortality and decreased survival time. Significantly increased mortality and decreased survival time was seen in mice exposed daily for 5 days to 100 mg/m³ A-C 24 hours before or after challenge with influenza virus.
- Twenty 3-hour exposures, 5 days/week, to 50 mg/m³ A-C followed immediately by challenge with influenza virus resulted in significantly increased mortality and decreased survival time in experimental mice compared to controls.

Studies of the effects of inhalation of A-C on formation of antibody and on pre-formed antibody are also in progress at IITRI. Mice were exposed 3 hours 5 days/week to 100 mg/m³ A-C before or after vaccination with influenza A₂/Japan virus. At various time intervals after vaccination, the mice were challenged with homologous influenza virus and mortality, survival rate, pulmonary consolidation and immune response were measured. The results obtained to date indicate that significantly decreased survival time and increased pulmonary consolidation occurred in many groups of vaccinated mice exposed to pollutant compared to vaccinated controls maintained in clean air. The primary and secondary immune responses, as measured by hemagglutination-inhibition and serum-neutralizing antibody levels and immunoglobulin concentrations are being evaluated.

The effects of acid aerosols on various animal models are being studied at the University of California, Davis. In these series of experiments the initial studies will utilize pathogen-free rats, while later studies will use macaque monkeys. These primates will be employed to validate the data from rats in a species phylogenically and anatomically closer to man and to approach the problem of pulmonary physiological studies on a larger species using more refined methods.

Results will be evaluated using physiological, morphological and biochemical techniques. Clearance of airways will be evaluated using tantalum bronchography and inhalation of radiolabelled particles followed with an Anger camera. Morphological evaluation will include use of light, transmission electron, and scanning electron microscopy, histochemistry, and autoradiography. Biochemical techniques are used to study the rate and pattern of synthesis of glycoproteins.

Morphological and histochemical studies were conducted with monkeys which were exposed to 250-450 mg/m³ of H₂SO₄ continuously for 7 days. The animals were sacrificed and multiple sections of lung, trachea, and nasal septum were examined by light microscopy. Sections from these exposed animals were essentially indistinguishable from normal, unexposed animals. Some of the guinea pigs exposed to a mean mass concentration of 25-29 mg/m³ for 7 days had paucity of cilia and cilia which were shorter than normal. This effect was more pronounced at points of airway bifurcation.

Biochemical studies resulted in a new culture technique for maintaining tracheal tissue in organ culture viable for up to 5 days. Using this new culture system, tracheal tissue from guinea pigs continuously exposed to 40 mg/m³ of fine H₂SO₄ aerosol for 6-8 days. No significant increase in incorporation rates for leucine nor glucosamine at 24 hours was observed although a trend toward an increase was evident. Only a small number of animals were studied.

Microbiological experiments were conducted to determine the influence of H₂SO₄ aerosols on immunological response and susceptibility of mice to respiratory infections with viruses. Tracheal organ cultures and alveolar macrophage cultures were prepared to measure the effect of H₂SO₄ on interferon production. The interferon titers of macrophage cultures from exposed mice appeared to be lower than those of control cultures. No difference in interferon production in tracheal organ cultures was reported. At the present time, immunoglobulin and albumin levels in lung lavages of mice exposed to sulfuric acid aerosol is being determined.

Research in the area of respiratory physiology was devoted to three studies: (1) baseline data on pulmonary function of non-human primates, (2) static pulmonary mechanics and lung volumes of guinea pigs exposed to sulfuric acid aerosol, and (3) pulmonary mechanical reflexes of guinea pigs before and after H₂SO₄ exposure. The exposed guinea pigs appeared to have greater EEV, a lower compliance despite a tendency to have larger lung capacity, decrease in respiratory frequency, and a decrease in minute volume.

The University of Washington is conducting research on behavior and respiratory effects of oxides of sulfur-aerosols mixtures. The first task is to determine the interrelationship between SO₂ and sodium sulfate or ammonium sulfate, and various physical environmental variables (humidity and cold) on respiratory function of guinea pigs. The investigators are presently completing studies on the threshold effect of SO₂/sodium chloride aerosol at 80% R.H. and 22°C. The results indicate that a certain fraction of the population studied is sensitive and responds to the pollutant. The response does not appear to be dose-related.

The second objective is to develop a quantitative, predictive model for assessing the role of ammonia and physical environmental factors on the oxidation of SO_2 , SO_3 , and SO_4 salts or acid aerosols. Mathematical modeling of the aerosol system, including H_2SO_4 and NH_3 , at concentrations expected to exist in the lung have been performed to estimate the time necessary for ammonia to react with the H_2SO_4 . The reaction times are strongly dependent on the H_2SO_4 mass concentration, ammonia concentration, aerosol size distribution and relative humidity.

The third objective is to determine the respiratory physiologic effect of exposure to sulfates and/or acid aerosols on human volunteers and to correlate their response to that observed in guinea pigs. Eight volunteers have been studied. The functional measurements include: (1) pulmonary flow resistance and compliance, (2) total respiratory resistance, (3) maximal and partial expiratory flow, (4) closing volume and (5) lung volume. There were no significant differences between the control and exposed group when the data were analyzed. However, two individuals did show an increase in resistance during the SO_2 - NaCl at high relative humidity. The investigators in this project have just begun to study patients with chronic respiratory disease. Three exposure modes will be used: (1) SO_2 alone at high relative humidity (RH), (2) SO_2 - NaCl aerosol at low R.H. and (3) SO_2 - NaCl aerosol at high R.H.² The concentration will be 1.0 ppm SO_2 and 1.0 mg/m³ of NaCl.

Epidemiological studies carried out by the Health Effects Research Laboratory have indicated that levels of suspended sulfates associated with certain adverse health effects were lower than the levels of sulfur dioxide and total suspended particulate associated with the same health effect. In addition, results of these studies indicate that suspended sulfates are the pollutants most consistently associated with the aggravation of asthma. Research in this area is continuing and will focus on ambient levels of sulfuric acid when reliable data on this pollutant became available in sufficient volume to permit thorough study.

● In-Use Catalyst Research

The primary objective of the in-use catalyst vehicle study being carried out by an EPA grant to the State of New York is to measure the emission of sulfuric acid aerosol from a population of catalyst vehicles as they accumulate mileage in normal use. At approximately 5,000 mile intervals, each vehicle will undergo a comprehensive emissions test consisting of the following sequence: (1) a 1975 Federal emissions test cycle (FTP), (2) a one-hour 50 mph steady cruise, and (3) a series of up to five tests following a "sulfate driving cycle" developed by the EPA. In addition to measuring carbon monoxide, hydrocarbons, nitrogen

oxides, O_2 , and SO_2 , a dilution tunnel with isokinetic sample probes will be used to collect filter samples for sulfuric acid and total particulate mass measurements from each test segment. Analysis of particulate sulfate mass is performed by the barium chloranilate (BCA) method, and x-ray fluorescence for mass emission rates of ten selected elements: lead, sulfur, phosphorous, platinum, calcium, silicon, copper, aluminum, zinc, and iron. Fuel economy is measured by carbon balance technique, and between test intervals by an in-line totalizing fuel meter that will be installed on each vehicle. Tank fuel will be collected at each test and analyzed for trace components, especially sulfur. Prior to each test, each vehicle will be diagnostically examined for tune-up condition, although no maintenance will be performed. Most of the vehicles to be studied have been solicited from organizations in the Albany area, but privately owned vehicles are being incorporated to expand the population and assess personally owned vehicular types.

The data collected from this study will be useful in determining the emissions values to be used in modeling the sulfuric acid emission rate from in-use catalyst vehicles. Several other correlations will also be calculated, apparent, particularly the relation of sulfate emissions to vehicular age, to fuel composition, and to carbon monoxide and hydrocarbon emission rates, as all three of these factors are directly related to catalyst activity. Testing is now under way; preliminary data indicate very low H_2SO_4 emissions of approximately .003 g/mi. Regulated emissions, however, appear to be in excess of national standards; this trend will be closely watched as the project continues.

E. Office of Mobile Source Air Pollution Control/Washington, D.C.

The sulfuric acid emissions from current production and prototype vehicles vary greatly as shown in Table XI.

The most important parameter in the formation of sulfuric acid emissions appears to be the oxygen level in the exhaust gas to the catalyst. The significant difference in sulfuric acid emissions between the catalyst-equipped vehicles with and without air injection is attributed to this oxygen level effect.

Current technology which has demonstrated low (below 10 mg/mi) sulfuric acid emissions has also demonstrated the capability to certify at the California emission levels of 0.9 HC, 9.0 CO, and 2.0 NO_x gm/mi. About 20 percent of the estimated sales for 1976 in California have non-catalyst or catalyst without air injection control systems. Prototype three-way catalyst-equipped vehicles, which also have low sulfuric acid emissions, have been successfully operated to 50,000 miles at emission levels below the California levels.

The most promising future sulfuric acid control technique is control of the exhaust gas oxygen levels by improved fuel metering systems and/or improved air injection systems. Oxidation catalyst, three-way catalyst, and dual catalyst emission control systems are all compatible with oxygen level control systems. Other important control techniques may be developed as sulfuric acid control system development programs are commenced. Most of the experimental work which has been done to date has been related to the characterization of production emission control systems, and relatively few data are available on advanced systems, especially those designed with sulfuric acid control in mind.

However, meeting standards more stringent than 0.9 HC, 9.0 CO, 2.0 NO_x gaseous emissions while controlling sulfuric acid emissions is not precluded. The degree of difficulty in meeting more stringent HC and CO emissions may be increased, depending on the control techniques used.

The advantages of improved air injection or improved fuel metering are not very apparent until standards of 0.41 HC and 3.4 CO along with H₂SO₄ emission standards are required to be met. This is because air injection is considered more likely to be used to meet these more stringent HC and CO standards.

The lack of a finalized test procedure for sulfuric acid emissions and the lack of a sulfuric acid emission standard have caused some manufacturers to defer from starting serious development programs. The test procedure is still being developed by EPA. Variability in test results over the sulfuric acid test cycle, the SC7, has continued to be

TABLE XI

**Sulfuric Acid Emissions from Baseline
Program Vehicles**

<u>Type of Emission Control System</u>	<u>Sulfuric Acid Emissions, mg/mi*</u>	
	<u>Range</u>	<u>Approximate Mean</u>
Non-catalyst	0 to 3	1
Oxidation catalyst w/o air injection	0 to 118	8
Oxidation catalyst w/air injection	0 to 123	30
3-Way catalyst	0 to 2	1

*Milligrams per vehicle mile on the sulfuric acid test procedure, the SC-7 with 300 ppm sulfur in the fuel. A milligram is one one-thousandth of a gram, or about 0.00004 ounces.

a problem for EPA and the manufacturers. This problem is expected to be alleviated as more is learned about sulfuric acid emissions and as the test procedure is standardized.

The following conclusions have been reached based on studies of the available data:

- Control of sulfuric acid emissions from automobiles is still in the infant stage of development. Many techniques and approaches for controlling sulfuric acid emissions remain to be explored.
- Domestic manufacturers are somewhat ahead of most foreign manufacturers in preparing to meet sulfuric acid standards.

The clear message from the responses to EPA's request for information on the studies of sulfuric acid emissions from the majority of the foreign manufacturers was that they are waiting to see what final test procedures and standards will be proposed before they mount an effort to meet the standards. Some of the foreign manufacturers do not even have the test equipment needed to measure sulfuric acid emissions, let alone have data and rational development plans, though in fairness, some foreign manufacturers, particularly Toyota and Nissan, have made significant contributions to the understanding of sulfuric acid emissions despite the long lines of communication between EPA and their research centers.

- Some manufacturers appear to be concerned about the variability of test results, and will probably maintain that EPA has no business setting standards until the test results are less variable.

It is true that the test procedures for sulfuric acid testing are relatively new and that some important parts of the feasible certification procedures currently remain to be finalized (especially the vehicle preconditioning). However, test result variability for both gaseous emissions and sulfuric acid emissions has always been a combination of both test procedure variability (driver, sampling, analyses, etc.) and vehicle variability (the vehicle does not perform exactly the same way on each test). The manufacturers always strive to reduce vehicle variability, and based on their comments and EPA's own work, EPA strives to reduce test variability. This has always been the case with gaseous emissions and will likely continue to be the case with sulfuric acid emissions, although it is true that the causes of vehicle variability during sulfate testing are relatively unexplored now.

- The analyses conducted in concert with this study resulted in estimates as shown below of the sulfuric acid emission levels that could possibly be met for various concurrent gaseous emissions standards projecting from current emission control knowledge.

At this point in time, the best estimates that can be given involve the use of ranges. There are four basic reasons for this: (1) The technology for controlling sulfuric acid emissions is just now being considered for development. (2) There is variability in the test results now and the test procedure is still not finalized. (3) Several different technical approaches could be used to meet the gaseous emission standards and their likely sulfuric acid emissions are not the same. (4) Not many sulfuric acid emission data are available from advanced gaseous emission control systems that were designed without consideration for sulfuric acid emissions, let alone systems that were designed with sulfuric acid emission control in mind.

As time goes by and the technology and understanding advances, the ranges will, of course, narrow.

The deterioration factor assumed for the sulfuric acid emission levels is 1.0 to reflect maximum sulfuric acid emissions at the 4,000 mile point. The lower bound of the sulfuric acid emissions in Table VII represents the lowest technically achievable standard for sulfuric acid at the given gaseous emission standard. Thus this maximum effort for sulfuric acid control is assumed to force three-way catalyst technology at the 0.41 gm/mi HC levels and no catalyst or low excess air-plus-catalyst technology at the 0.9 gm/mi HC levels. This estimate would involve the greatest effort on the part of the manufacturers. This also means that it will be more difficult to certify at both the given gaseous and sulfuric acid levels. The highest level in the range assumes only moderate technological improvements and leaves more technological options open to the manufacturer. This highest level also involves a much lower risk of all manufacturers being able to certify. These ranges include lead time, variability, and technological considerations; however, it does not mean that all currently produced emission control systems of each manufacturer will be capable of certification.

Table VII should not be interpreted to mean that low gaseous emission levels cannot be achieved along with low sulfuric acid emissions. Three-way catalysts have the potential to do both. Also, other technologies, particularly limited oxidation catalyst approaches are still relatively unexplored. What should be interpreted from Table XII is that it would be more difficult for the manufacturers to certify vehicles at both stringent sulfuric acid and gaseous emission standards.

TABLE XII

Ranges of Sulfuric Acid Emission Levels at Various
Gaseous Emission Standards

Gaseous Emissions g/mi, 1975 FTP			Sulfuric Acid Emissions mg/mi, sulfate test cycle
<u>HC</u>	<u>CO</u>	<u>NO_x</u>	<u>H₂SO₄</u>
1.5	15	3.1	5-15
1.5	15	2.0	5-15
0.9	9.0	2.0	5-15
0.9	9.0	1.5	5-15
0.41	3.4	2.0	5-50*
0.41	9.0	1.5	5-50*
0.41	3.4	1.0	5-50*
0.41	3.4	0.4	5-50*

*The lead time for the introduction of three-way catalysts by all manufacturers and the 50,000 mile durability of three-way catalysts at these gaseous emission levels is uncertain.

It should be recognized that, as with emission control systems for regulated gaseous emissions, EPA does not dictate the control technology to be used to control sulfuric acid emissions. That choice is left to the individual vehicle manufacturers. EPA only establishes the level that the manufacturers' vehicles are required to meet for each pollutant.

The general technical approaches now under study for controlling sulfuric acid emissions appear to be improved fuel management, control of oxygen level in the exhaust, and catalyst modifications. The approaches listed above are similar to some of those also being pursued for control of gaseous emissions control at more stringent gaseous emission standards.

III. DISCUSSION OF PROGRAM HIGHLIGHTS

The two events during the reporting period which most influenced the priorities and pacing for the CRP's activities were, first, the announcement by EPA in the spring of 1975 that the Agency was considering a notice of proposed rulemaking for an automotive emission standard for sulfate and, second, the subsequent announcement about one year later that there would be no regulatory action at least for the 1979 model year vehicles. The initial announcement of intent provided the impetus for a heavy involvement of the Agency's emission characterization resources toward development of a sulfate test cycle. This effort resulted in a tentative test cycle for possible use by EPA's certification group should an emission standard become effective.

Concurrent with the test cycle development was the continuation of characterization of both regulated and nonregulated emissions of prototype and production catalyst-equipped light-duty vehicles. Work conducted under this portion of the CRP during the reporting period resulted in data which showed the emissions of sulfuric acid from catalyst-equipped vehicles to be substantially less than originally predicted: 1975 vehicles designed to conform to California standards (air-pump-equipped) emitted approximately .035 g/mi H_2SO_4 ; catalyst-equipped vehicles designed to conform to Federal (49-state) standards emitted approximately 0.015 g/mi H_2SO_4 . Details of these studies may be found in Supplements I and III.

In the fall of 1975, EPA participated in a General Motors roadway experiment designed to determine sulfuric acid emissions factors and resultant ambient air concentrations of sulfuric acid from a fleet consisting entirely of air-pump-equipped catalyst vehicles designed to meet 1975 California standards. Results of this dispersion experiment which took place during October 1975, showed the vehicles' average emission rate of sulfuric acid to be approximately .035 g/mi, confirming earlier dynamometer test results. At the same time, results of ambient measurements including SF_6 tracer studies indicated that the dispersion model (EPA HIWAY Model) which had been previously employed to predict near-roadway sulfuric acid concentrations overpredicted such concentrations under the most adverse meteorological conditions. The tendency of the model to over-predict concentrations near a line source, together with the confirmation of dynamometer test data to show lower emissions of H_2SO_4 than had earlier been predicted, largely provided the basis for EPA's decision in the spring of 1976 not to take action with regard to establishing a motor vehicle sulfate emission standard for at least the 1979 model year vehicles.

During the General Motors sulfate dispersion experiment, measurements of particle size of ambient particulate were made both inside a car on the roadway and a short distance downwind of the roadway. These measurements, together with concurrent determination of sulfuric acid levels, led to the conclusion that the sulfuric acid emitted from the catalyst-equipped vehicles in the study was predominately in the size range of 0.01 to 0.1 μm diameter. The contribution of near-roadway sulfuric acid from catalyst-vehicles was found to be approximately 5 $\mu\text{g}/\text{m}^3$.

The finding that catalyst-equipped vehicles can emit ultrafine sulfuric acid aerosols may significantly affect the direction of EPA's health effects research on sulfates -- sulfuric acid in particular. Research now under way employs particles of sulfate/sulfuric acid in the size range of 0.3 μm in diameter, which is the most prevalent form of aged sulfate aerosol in ambient air. However, the much smaller particle of the in-roadway and near-roadway H_2SO_4 emanating from catalyst-equipped vehicles may have an entirely different action upon the human respiratory system. It is hypothesized that this ultrafine aerosol may penetrate deeper into the lung than the larger 0.3 μm respirable size sulfate aerosol now being studied. More information is being gathered with regard to the physical and chemical properties of the sulfuric acid emitted from catalyst-equipped vehicles that is found near roadways. This information, along with the development of technology for generating and measuring ultrafine sulfuric acid aerosol will be employed in the design of future toxicological and clinical health effects research. In-roadway studies will also be conducted to assess the health risk of commuter populations exposed to the ultrafine sulfuric acid aerosol.

New vehicles were used to collect data on sulfuric acid emissions because: (1) Data could be gathered quickly for use by the Agency in making decisions regarding regulation of emissions for those vehicles. (The first available vehicles were employed which had little or no mileage accumulation prior to testing). (2) The use of low-mileage vehicles eliminates variables such as maintenance, type of fuel, and operating mode which can significantly affect the volume and composition of vehicular emissions.

In an effort to determine how emissions vary from new vehicles to those actually operated by the consumer, and to determine ambient air concentrations resulting from such vehicular emissions in the real world, EPA is conducting several studies:

1. The Los Angeles Catalyst Study (LACS) has been in operation since 1974 on a major freeway in Los Angeles to measure upwind and downwind concentrations of many pollutants. Since the meteorological conditions at this site are such that the wind is perpendicular to the roadway a major portion of each day, the vehicular contribution to the ambient air may be calculated by subtracting levels of pollutants downwind from those found upwind. Hi-vol data resulting from these measurements show a statistically significant increase in sulfates -- roughly 5 $\mu\text{g}/\text{m}^3$ downwind of the freeway. What portion of this increase may be attributed to catalyst-equipped vehicles, heavy-duty vehicles, or artifact formation on collection media is not yet established. Continuing analysis of the data available, together with adjunct experiments to identify the source of the sulfate contribution, are now in progress. Recently developed sulfuric acid specific samplers

will be employed at the site when available to determine what portion of the sulfate concentration is sulfuric acid, and the levels to which populations on and near the roadway would be exposed.

In support of the LACS two separate studies were established on unburned fuel: (1) the National Fuels Surveillance Network (NFSF), and (2) the Unleaded Gasoline Enforcement Program. In the NFSF, samples of all grades of gasoline from the ten EPA regions were collected and analyzed for sulfur. Additional samples from California were also collected in the San Francisco and Los Angeles metropolitan areas over a three-month period for subsequent sulfur analyses. In the United Gasoline Enforcement Program, samples are collected and analyzed for the regulated elements lead (Pb) and phosphorus (P), which are both harmful to catalyst operation. Data were obtained on the number of samples by region which exceeded the 0.05 g/mi regulation for Pb and the 0.005 g/mi regulation for P.

The ongoing quality assurance programs for the LACS and the Fuels Program have maintained close control on the output data quality. A combination of internal quality control procedures during sampling and analysis, plus an active external audit program, provide continuing assessment of data validity. A short-term study has also been completed to determine the reproducibility of LACS hi-vol measurements on a 24-hour basis.

Animal toxicology studies of sulfuric acid aerosol are under way by EPA with both in vivo and in vitro systems; human clinical studies are being planned. Experiments to date have employed aerosols with particles in the size range of 0.3 μ m diameter most commonly found in ambient air. To date, there are insufficient data from animal studies to show that sulfuric acid at concentrations comparable to actual or projected ambient levels evoke adverse biological responses. Studies of chronic exposure and studies of effects of interaction between sulfuric acid and other ambient air pollutants, however, are still in progress or in the planning stages. At this time there is still insufficient information available to determine conclusively whether sulfuric acid in the 0.3 μ m diameter size range most common to ambient sulfate aerosol is a threat to public health.

The findings from the GM dispersion study that sulfuric acid emitted by catalyst vehicles may be an order of magnitude smaller in particle size than aerosol which is "aged" (that is, dispersed over a period of time in the ambient atmosphere) has spurred an interest in conducting health effects research on sulfuric acid aerosol in the smaller particle size range of 0.01 to 0.02 μ m diameter. Such studies will not be initiated, however, until (1) further investigation is made to identify both the physical and chemical properties of roadway and near-roadway sulfuric

acid aerosol resulting from catalyst vehicular emissions and the average ambient concentrations, (2) reliable and accurate means of generating sulfuric acid aerosol in the 0.01 to 0.02 μm diameter size range and maintaining a given concentration level for laboratory experiments is developed, and (3) reliable and accurate measurement techniques for monitoring concentrations of the "ultrafine" aerosol are developed.

Until the required instrumental techniques are developed and further information on the characterization and quantification of the ambient ultrafine aerosol becomes available, health effects research will continue to focus on the larger (approximately 0.3 μm) particle size aerosol. Clinical studies of human exposure to this size particle are still in the planning stage and are scheduled to be initiated during FY 1977. Health effects research will be performed on the "ultrafine" sulfuric acid aerosol as soon as the technology is available.

Sulfuric acid, though a major focus of the Catalyst Research Program, has not been the only emission product of concern. When the Catalyst Research Program was first initiated, there was considerable concern over the possibility of platinum and/or palladium emissions from the degradation of oxidation catalysts. Although these two noble metals form the active components of the oxidation catalyst, very little was known about health effects of the two metals.

Information from occupational exposure to platinum and palladium gave cause for concern that any emission of platinum or palladium could constitute a "new" environmental pollutant. Although the chemical composition and concentrations of any platinum compounds emitted were unknown, concern for public health spurred the initiation of a broad program of health effects research on platinum and palladium with a focus on platinum, which constituted the major portion of the catalyst material. Efforts to determine the toxicity, carcinogenicity, mutagenicity, cytogenicity, allergic properties, and effects on immune response were begun in FY 1975. Most research efforts concentrated on platinum sulfate because it was predicted that soluble compounds would be more likely to produce adverse health effects, and because sulfate concentrations were known to be present in exhaust from catalyst-equipped vehicles.

Concurrently, with the health effects research, efforts to identify and quantify noble metals both in exhaust and in environmental and biological matrices were initiated. Studies of existing levels of platinum in human populations and in environmental media (air, soil, water), were undertaken to establish a pre-catalyst baseline for comparison with later data for emissions from automotive catalysts. Additional research was directed toward improving analytical methodologies for measuring low levels of platinum and palladium in a variety of matrices.

A conference was held in December 1975 to bring together those involved in the many areas of platinum research undertaken by the CRP. The purpose was to review progress made, to identify research gaps, and

to set priorities for future research. Results reported at the conference were as follows:

- Baseline studies showed that no reasonable quantities of Pt existed in air, soil, or water.
- Occupational exposure levels were reported to be approximately 0.02 to 0.2 $\mu\text{g}/\text{m}^3$.
- Human burdens determined by examination of urine, blood, hair, and feces showed no measurable Pt in any individual, though pooled blood samples showed minute quantities.
- Autopsy data showed that a major proportion of individuals studied had measurable amounts of Pt in varying types of tissue.
- Exposure to 0.02 $\mu\text{g}/\text{m}^3$ to 0.2 $\mu\text{g}/\text{m}^3$ or higher levels can result in measurable levels of Pt in urine.

Preliminary results from the GM study, reported by GM after the Pt review conference, showed ambient concentrations of platinum as high as 0.03 $\mu\text{g}/\text{m}^3$, a concentration which exceeds the lower values reported for occupational levels.

Characterization of catalyst-equipped vehicular emissions showed no measurable quantities of platinum in either the fine particulate or gaseous fractions of exhaust; large particulate was found to contain small amounts of platinum, but the platinum compound remained undetermined. No accurate emission factors can as yet be calculated because analytical methods needed to perform this work are not yet fully developed.

It has been shown that some platinum compounds can be methylated under laboratory conditions via the same vitamin B₁₂ mechanism through which mercury is methylated; consequently research should continue in order to determine whether platinum emitted from catalyst vehicles, however small in quantity, is biologically active.

Acute toxicological studies showed that the toxicity of platinum compounds appears to be a function of the solubility of the compound. Therefore, any process in the environment which might involve biotransformation resulting in soluble platinum compounds is of concern. Chronic and long-term health effects studies on platinum compounds, such as carcinogenicity, are still under way. Results of these studies can be important in influencing the research priorities.

Other emissions from catalyst-equipped vehicles are also under study. Since a manganese compound is now being used as a substitute for TEL, compounds which are likely combustion products of the manganese additive are scheduled for toxicological evaluation during FY 1977. Other new fuel additives which may affect catalyst emissions, and any new catalyst formulations which employ elements or compounds for which insufficient data exists to make a health effects assessment, will be investigated. For example, health effects studies are planned in FY 77 on ruthenium which is under consideration for use in reduction catalyst systems.

APPENDIX A
Crosswalk Listing of FY 1975 Projects
by
Laboratory and Tasks

FY 75 ROAP 21BCE
Health Effects Research Laboratory (RTP)

TASK	TASK OBJECTIVE	STATUS
005	Estimate no-effect level using mouse pulmonary infectivity model (a) of appropriate Pt-group metal compounds administered singly; and (b) of base metal compounds administered in appropriate combination	Ongoing
006	Compare relative toxicities of Pt-group compounds against Pb compounds using <u>in vitro</u> macrophage system	First year completed; second year cancelled due to nonproductive results
007	Compare relative toxicities against Pb compounds using <u>in vitro</u> conjunctival cell and respiratory epithelial cell cultures -- of Pt-group compounds	Catalyst Program work terminated due to lack of progress; some work on system continuing in CSD/HERL/RTP
008	Estimate no-effect level of Pt-group metal compounds using immediate and delayed allergic response in animals	Ongoing
009	Compare relative cytogenicity against Pb compounds using <u>in vivo</u> hamster system (a) of Pt-group compounds (b) of base metal compounds	See Tasks 015 and 016
010	Determination of the relative mutagenicity of Pt compounds by mammalian cell culture and plant embryo techniques	Ongoing
011	Compare relative toxicities against Pb compounds using biochemical parameters (a) of Pt-group compounds, (b) of base metal compounds	Completed

TASK	TASK OBJECTIVE	STATUS
012	Compare pulmonary carcinogenicity of Pt-group metal compounds and of Pb compounds in association with polynuclear aromatics using <u>in vivo</u> hamster system	Ongoing
014	Effects of chronic of intermittent exposure to low levels of major catalyst attrition products or their decay products on human pollutant burdens	Completed
015	Effects of Task 014 on irritation symptoms in humans	Never implemented; occupationally exposed subjects not available for epidemiologic assessment due to lack of cooperation by Pt refinery companies
016	Assessment of subtle physiologic changes induced by exposure to major catalyst attrition products or their decay products, enzyme changes, immunologic deficits, chromosomal aberrations	Ongoing
022	Comparative methylation chemistry of Pt-group metals, selected base metals, and lead with subsequent toxicological assessment of stable metallic compounds	Completed; further chemistry & toxicological evaluation of methylated Pt compounds to be done in combination FY 75-76 work
025	Analysis of animal tissue for platinum, palladium, lead, and manganese	Completed
031	Public health impact of suspended particulate sulfates	Lead responsibility HERL/RTP; ongoing outside CRP
032	Public health impact of suspended particulate sulfates	Lead responsibility HERL/RTP; ongoing outside CRP

TASK	TASK OBJECTIVE	STATUS
033	Analysis of tissue samples collected throughout CHES network to assess population pollutant burdens of Pt, Pd, Ru, and Al	Completed; second phase "Research and Development of Analytical Methods for Measuring Trace Element Emission & Attrition Products on Mammalian Tissue" ongoing
034	Clinical studies of human response to noble metals	Never initiated.
035	Effect of controlled exposure to H ₂ SO ₄ aerosol on immune response	Ongoing
036	Effect of particulate sulfates and noble metals on human behavior	Never initiated; animal work ongoing - see Task 081
037	Effects of ambient exposure to selected chemical particulates on the occurrence of carcinogenic or mutagenic effects	Never initiated; see Task 012 for related effort
038	Clinical studies of cardiopulmonary effect of H ₂ SO ₄ aerosol	Ongoing
075	Toxicological evaluation of airborne respirable particulates and mists	Ongoing
081	Development of sensitive biochemical and behavioral indicators of trace substance exposure	Ongoing
082	Characterization and measurement of regulated sulfates and particulate emissions from in-use catalyst vehicles - 1975 national standard	Ongoing

TASK	TASK OBJECTIVE	STATUS
083	Analysis and evaluating photodynamic bioassay data on organic extracts of particulate atmospheric pollutants collected by the National Air Sampling Network	Ongoing
089	Toxicological evaluation of emissions from diesel engines	Ongoing; joint effort between HERL and ESRL
090	Study the effects of inhaled sulfates above and in combination with SO ₂ on pulmonary defense mechanisms	Ongoing

FY 75 ROAP 26AAE
Health Effects Research Laboratory (RTP)

TASK	TASK OBJECTIVE	STATUS
025	Exposure of tissue culture systems to pollutants under conditions simulating physiologic studies of lung and conjunctiva	Initial work nonproductive; being continued with some improvement of set up of system in CSD/HERL/RTP
026	Assessment of fuel additive emissions toxicity via selected assays of nucleic acid and protein synthesis	Completed

FY 75 ROAP 218CE
Environmental Monitoring and Support Laboratory

TASK	TASK OBJECTIVE	STATUS
023	Monitor air quality along a major highway in southern California. Utilizing existing methods, analyze water soluble sulfate, lead, and TSP at 4 sites and CO at 1 or 2 sites. Additionally, 1 meteorology station will be established.	Completed
024	Monitor air quality along a major highway in southern California. Utilizing existing methods, analyze water soluble sulfate, lead, and TSP at 4 sites. Additionally, 1 meteorology station will be established and total motor vehicle count (not vehicle mix) at 1 site will be made.	Completed
055	Commercial fuels collection and analysis.	Ongoing
056	Standardized methods for measurement of and collection and analysis of particulate sulfates	Ongoing
057	Quality assurance guidelines for measurement methods applicable to mobile sources and fuels and fuel additives	Ongoing
058	Development of standard reference materials for emissions from mobile sources and fuels and fuel additives	Ongoing
059	Collection and analysis of samples at selected sites including sulfates, trace metals, and nitrates	Ongoing
060	Collection and analysis of samples at selected sites, including sulfates, trace metals, and nitrates	Ongoing

TASK	TASK OBJECTIVE	STATUS
061	Determination of various pollutants in TSP, fine particulates, and soil samples	Ongoing
062	Maintain national sample bank and implement data acquisition and processing system	Ongoing
063	Expand network for collection and analysis of fuel samples specifically in southern California in support of catalyst field program	Ongoing
064	Survey and evaluate analytical methods pertinent to Tasks 065 and 066	Completed
065	Standardized methods for measurement of exhaust and ambient sulfates	Ongoing
066	Standardized methods for noble metals and catalyst support materials	Ongoing
067	Develop standard reference materials for mobile source pollutants measurements	Ongoing
068	Conduct interlaboratory performance surveys for sulfate and catalyst-related particulates	Ongoing
069	Monitor air quality along a major highway in southern California. Utilizing existing methods analyze water soluble sulfate, lead, & TSP at 4 sites and CO at 1 or 2 sites. Additionally, 1 meteorology station will be established and total motor vehicle count (not vehicle mix) at 1 site will be made.	Completed

TASK	TASK OBJECTIVE	STATUS
070	Inhouse & field evaluation of existing analytical sampling and analysis schemes pertinent to the determination of pollutants emanating from catalyst-equipped automobiles	Completed; FY 76 task specifically related to NH_4 and H_2SO_4 emanating from catalyst-equipped vehicles
071	Same as Task 069 with the addition of traffic mix data, TSP, size distribution at 1 station, 1 or 2 additional hi vols at a distance away from highway and of TSP samples.	Ongoing
072	Handling, validation, and interpreting data from southern California, and complex source studies, including report writing and computer costs	Ongoing
073	Monitor complex sources such as street canyons, shopping centers, and parking garages in southern California (e.g. Disneyland) for mobile source pollutants	Ongoing
080	Assist in sampling and analysis, baseline studies	Completed
085	Provide sample handling protocol for catalyst metal analysis of a massive dust sample collected at the LACS site	Completed
086	Develop and implement an operational system for evaluating and collaboratively testing methods recommended for air pollution	Completed
087	Perform x-ray fluorescence analysis of samples from the catalyst study	Completed
088	Develop an intervention time series model for the Los Angeles Catalyst Study	Ongoing

FY 75 ROAP 26AAE
Environmental Monitoring and Support Laboratory

TASK	TASK OBJECTIVE	STATUS
003	Promulgation of regulations for registration of fuels and fuel additives	Ongoing
004	Initial registration of designated additives and fuels	Ongoing

FY 75 ROAP 21BCE
Environmental Sciences Research Laboratory

TASK	TASK OBJECTIVE	STATUS
001	Study gaseous and particulate emissions - California 1975 model year vehicles	Ongoing
002	Characterize particulate emissions, prototype catalyst cars	Ongoing
003	Visibility effects - catalyst and non-catalyst advanced prototype systems	Completed
004	Develop methodology to determine the effect of gasoline composition and additives on emissions control device performance	Completed
027	Validation of highway gaseous dispersion model for simulation of air quality	Completed
028	Conduct wind tunnel experiments to evaluate current highway model for gaseous emissions; monitor Tasks 029 and 30, prepare reports	Not initiated; work plans in process to do study for derived diffusion coefficients near highway wake structure
029	Evaluate applicability of highway gaseous dispersion model for mobile source particulate and aerosol species	Ongoing
030	Develop and evaluate dispersion model for complex mobile sources	Not initiated
039	Analysis of "unusual" emissions from current and future mobile sources -- impact of control devices	Ongoing
040	Atmospheric chemistry of acid aerosols	Ongoing
041	Personal exposure meters for suspended sulfates	Ongoing

TASK	TASK OBJECTIVE	STATUS
042	Adapt methods for SO ₂ and SO ₃ to mobile source emissions measurement	Ongoing
043	Develop methods for total sulfur, sulfate, and other sulfur compounds in particulate emissions from mobile sources	Ongoing
044	Characterize particulate emissions from production catalyst-equipped cars	Ongoing
045	Operate dynamometer and test equipment in support of catalyst-related emissions method development and characterization studies	Ongoing
046	Procure test and data acquisition equipment in support of catalyst-related emissions testing program	Ongoing
048	Particle size, chemical characterization, formation and growth rates of scattering roadside aerosols	CRP work completed at LACS site
049	Study of scavenging of SO ₂ and sulfates by surfaces near roadways	Completed
050	Smog chamber study of SO ₂ photo-oxidation to SO ₄ under roadway conditions	Ongoing
052	Develop portable device for collection of sulfate and sulfuric acid	Ongoing

TASK	TASK OBJECTIVE	STATUS
053	Develop laboratory method for collected sulfate and sulfuric acid aerosols	Ongoing
054	Fabricate 12 portable samplers for measurement of sulfuric acid	Ongoing
078	Characterize particulate emissions - prototype catalyst cars	Ongoing
079	Characterization of roadside aerosols - particle size, chemical composition, formation, growth, and light scattering of roadside aerosols	Cancelled; ongoing in ESRL
089	Toxicological evaluation of emissions from diesel engines	Ongoing; joint effort between ESRL and HERL/RTP

FY 75 ROAP 26AAE
Environmental Sciences Research Laboratory

TASK	TASK OBJECTIVE	STATUS
007	Protocol to characterize gaseous emissions as a function of fuel and additive composition - prototype vehicles	Completed
008	Validate engine dynamometer test protocol for control system performance	Terminated, draft unacceptable; no present corresponding task
009	Protocol to characterize particulate emissions as a function of fuel and additive composition	Terminated, no present corresponding task
010	Operate engine dynamometer test facility	Terminated, no present corresponding task
011	Acquire equipment, provide contract services; operators, set-up, and maintenance personnel	Ongoing
012	Characterize current vehicle gaseous emissions	Completed
013	Characterize rotary engine emissions as a function of lubricant composition and fuel/lubricant interaction. Develop test protocol for nonregulated emissions therefrom	Cancelled
014	Characterize alternate power systems (rotary) gaseous emissions	Cancelled
017	Characterize particulate emissions - alternate power systems (rotary). Develop protocol.	Cancelled

TASK	TASK OBJECTIVE	STATUS
018	Characterize detailed gaseous and particulate emissions - non-catalytic advanced control prototype	Ongoing
019	Characterize diesel gaseous and particulate emissions	Ongoing
021	Develop predictive model for assessing effects of gasoline composition and additives on exhaust species in combustion reaction studies	Completed
023	Exploratory investigation of toxic and carcinogenic partial combustion products from various nitrogen-containing fuel components and gasoline additives	Completed
024	Exploratory investigation of the toxic and carcinogenic partial combustion product from various oxygen- and sulfur-containing fuel components and gasoline	Completed
028	Chemical ionization mass spectrometry of volatile lanthanide chelates; application of CIMS to analysis of metal chelates and other pollutants	Ongoing

FY 75 ROAP 21BCE
Health Effects Research Laboratory (Cincinnati)

TASK	TASK OBJECTIVE	STATUS
013	Toxicologic evaluation of whole engine exhausts from catalytic-controlled systems	Completed
074	Toxicology of respirable sulfur compounds	Ongoing
075	Toxicological evaluation of airborne respirable particulates and mists	Ongoing
076	Comparative inhalation toxicology specific to catalyst non-regulated emissions	Ongoing
077	Long-term, low-level, comparative inhalation toxicology specific to non-regulated emissions from oxidation catalysts	Ongoing

APPENDIX B

List of Supplements

- I. Health Effects Research Laboratory/Research Triangle Park, N.C.
- II. Environmental Monitoring and Support Laboratory/Research Triangle Park, N.C.
- III. Environmental Sciences Research Laboratory/Research Triangle Park, N.C.
- IV. Health Effects Research Laboratory/Cincinnati, Ohio
- V. Office of Mobile Source Air Pollution Control, Office of Air and Waste Management/Washington, D.C.